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TECTONIC ANALYSIS OF A MINING DISTRICT: PACHUCA, MEXICO.[1]

EDWARD WISSER.

ABSTRACT.

An ore guide is generally a combination of structure, mineral assemblage and host rock which suggests an outer portion, whether top, side, or bottom, of a setting enclosing an ore body.

Such a guide is empirical if the reason for its acceptance as a guide lies in the fact that ore has been found elsewhere in settings that look similar to the one in question, and so long as the underlying reasons for the preference shown by known ore for such settings are not understood. Use of empirical ore guides far from known ore is dangerous, for an ore setting in one district may have a meaning quite different from that of a similar-looking setting in another district.

Ore settings seen today are inert, but the history of ore formation is one of dynamic events: the ore solutions moved along their channels to the place where they deposited their load, and the walls of the fracture within which the ore body deposited often moved also, at the time the ore body was being deposited within them.

Deciphering this dynamic record, dominated as it was in many cases by tectonics, may be called *tectonic analysis*. The Pachuca silver district is used as an example of the use of this tool in exploration; but while knowledge of Pachuca tectonics has been painfully acquired over many years, an attractive possible application of tectonic analysis lies in the speedy evaluation of virgin districts.

ORE GUIDES.

AN ore guide is anything seen in the crust of the earth that suggests the proximity of hidden ore. It may indicate a general area potentially ore-bearing, or it may point specifically toward a possible ore body within such an area. An ore guide is commonly a combination of structure, mineral assemblage and host rock which suggests an outer portion, whether top, side, or bottom, of a setting enclosing an ore body or an ore district.

Such a guide usually suggests empirically ore to the mining geologist because ore has been found elsewhere in settings that look similar. If the proven and the potential settings are close together in the same district, the ore guide

[1] Presented before The American Institute of Mining and Metallurgical Engineers and the Society of Economic Geologists, joint meeting, St. Louis, Mo., Feb. 20, 1951.

although empirical may be trustworthy. But where the supposed ore guide appears in a district without known ore the use of analogy may be dangerous.

Ore settings today are inert, but they were scenes of activity at the critical time of metallization. The problem of ore localization is dominantly one of dynamics: the ore solutions moved into the place where their load was deposited. It is this writer's opinion, and that of others, that with many vein deposits the walls of the fissure or fault within which the vein-matter deposited spread apart or glided, one along the other, at the very time of vein formation. In other cases movement of the fracture walls took place before vein formation.

The nature and sequence of tectonic activity and its time relations to mineralization varied from district to district. A setting that exhibits the results of critical events in one district may resemble one that records a very different history in another district; the one may enclose ore, the other may be barren.

It follows that use of empirical ore guides is risky unless the dynamics of ore localization are deciphered. The problem can rarely be solved from study of the ore body itself and its immediate surroundings; but the solution often becomes manifest when the geologic history, especially the tectonic history of the critical period of metallization, of the district as a whole has been deciphered.

Dissection of a mining district in order to study the origin of its features of structure, mineralization, etc. from a tectonic standpoint and to observe the relation of these features to each other and to the district as a whole may be called *tectonic analysis*. Assembling the results into a consistent whole gives a tectonic synthesis, an integrated concept of the role of tectonics in producing the mining district as it appears today.

The notion that tectonic analysis can lead often to understanding of why ore is where it is hinges on the assumption that most ore bodies deposited under the influence of tectonic stress. Tectonic analysis is a valid exploration tool only to the extent that this underlying assumption is valid.

The ability to use tectonic analysis depends on a fundamental and broad grasp of the mechanics of rock deformation, a grasp seldom possessed by mining geologists. Study of rock deformation cannot be limited to the district in question. Rock deformation is a problem in itself: it must be studied wherever it occurs in the crust of the earth and in the laboratory.

Tectonic synthesis attempts to furnish *reasons* why ore favors the settings in which it is found; it attempts to go beyond empiricism, which merely seeks settings that look similar to known ore settings. If tectonic synthesis succeeds in this attempt it should aid in lifting mineral exploration from its present status as an art to its rightful position as a science.

Tectonic analysis and synthesis of the Pachuca silver district, Mexico, may serve to illustrate the above conceptions.

THE PACHUCA SILVER DISTRICT—GENERAL.

The Pachuca-Real del Monte silver district has been described by the writer (3, 5, 6, 7),[2] by Thornburg (2), by Bastin (1) and others. The present paper

[2] Figures in parenthesis refer to Bibliography at end of paper.

presents some ideas not appearing in earlier papers by the writer, since they spring from recent office re-study of data collected years ago. Earlier concepts are modified or denied by some present concepts.

The district (Fig. 1) is one of silver-bearing veins in Tertiary volcanics, mainly andesitic flows, tuffs, agglomerates, capped in places by rhyolite flows and tuffs, which in turn are overlain by dacite flows and agglomerates. Dikes and small stocks of quartz porphyry and dacite are abundant.

The metallization, which made Pachuca one of the great silver camps of the world, took place toward the close of a long and complex cycle of deformation, extrusion and intrusion. Tectonic stress, of one kind or another, was active throughout the cycle. The period of vein-formation was relatively short and sharp, and the process was simple and uniform throughout the district. Vein minerals deposited in a sequence that varied little from place to place; overlaps in time of deposition were common, but few vein minerals show multiple generations separated in time.

Hydrothermal activity commenced with alteration of the wall rock. The solutions involved passed up and along those fractures that existed and were permeable at the time. Alteration consisted of propylitization, with formation of chlorite, carbonates, epidote, etc., affecting nearly the whole district to greater or less degree; sericitization, more closely confined to the environs of the solution channels; and silicification, hugging the channel-fractures still more closely. Propylitization appears to have been the earliest process, followed by sericitization and silicification in turn, solutions of each type spreading outward and upward from the channels, one on the heels of its predecessor, but each successively travelling less distances into the wall rocks.

This alteration, especially the silicification, overlapped in time the formation of the veins; but the bulk of alteration had been accomplished by the time vein-formation was at its height. The system of vein-fractures continued to develop and multiply throughout the period of alteration and vein-formation; fractures that came into existence only during the later stages of vein-formation were born too late to be loci for strong hydrothermal alteration. In general the younger the vein-fracture, the less does it show sericitization and silicification of its walls.

The earliest vein minerals, coarse-grained gray or glassy quartz, massive pyrite, dark iron-bearing sphalerite, also invaded the permeable fractures they found at hand. Although the fracture system was growing and diversifying, in response to persistent regional deformation, the early vein-solutions utilized to a large extent the fracture-channels of the altering solutions so that veins exhibiting the early vein minerals characteristically show also strong alteration of their walls.

Next came the silver surge of metallization, depositing light brown sphalerite, galena, and argentite. The gangue of this surge was white, fine-to-medium-grained quartz with hypidiomorphic texture, rhodonite, and some calcite. The quartz is so typically associated with ore that it has been called the "productive" quartz. The bulk of the galena was deposited after the bulk of the quartz and sphalerite, and the bulk of the argentite was deposited after the bulk of the galena, but time relations were close during the silver surge, and in some veins

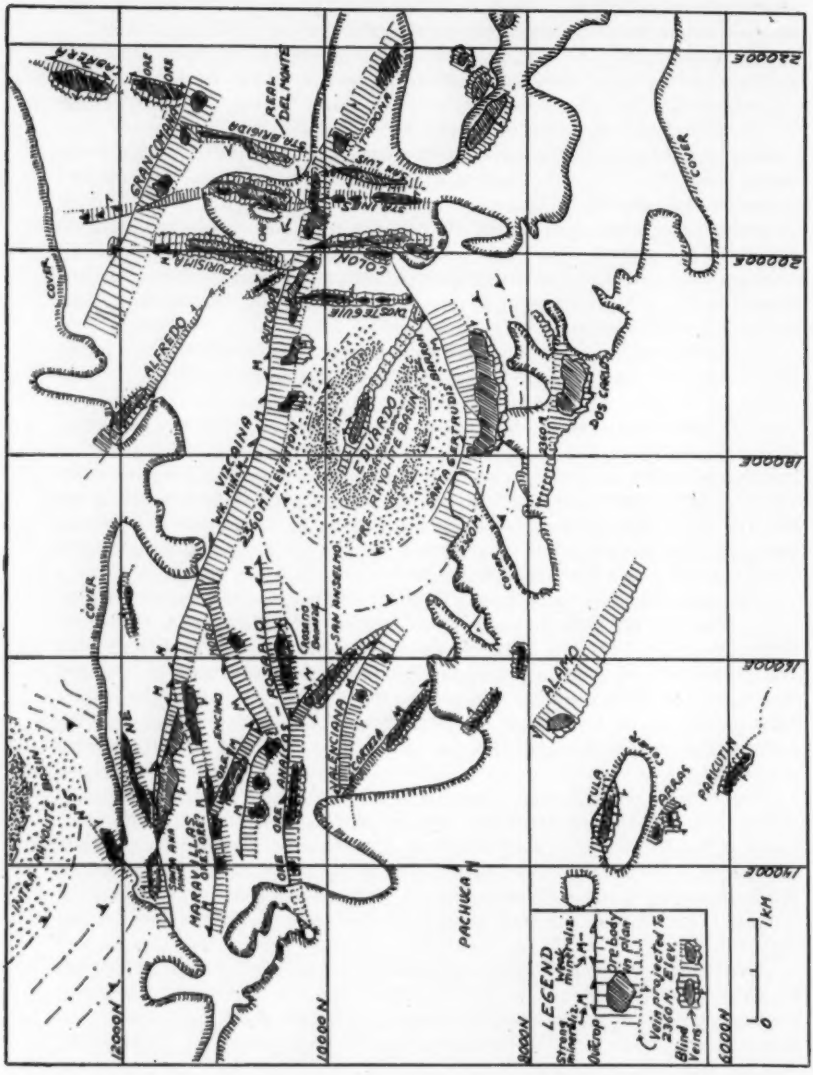

FIG. 1. Pachuca-Real del Monte Silver District, Mexico.

all minerals mentioned look essentially contemporaneous. Argentite however continued to be deposited, in some localities, after deposition of base sulphides had virtually ceased.

Solutions of the silver surge utilized in their turn fractures that were present and permeable at the time. Tectonic activity continued in ever varying forms. Of the older fractures sealed with early, barren vein matter, those suitably oriented under stress conditions prevailing during the silver surge were torn open to receive ore bodies, those not so oriented remained sealed. In central and southern Real del Monte and elsewhere fracturing and mineralization proceeded simultaneously: the mineralogy of a vein there reveals the precise stage of the mineralization cycle in which its vein-fracture formed. Thus, the great Purisima ore body (Fig. 1) deposited as the Purisima vein-fracture was forming (7, p. 285). Some of the youngest vein-fractures came into being too late to receive the bulk of the base sulphides and carry almost exclusively productive quartz and argentite.

EXPLORATION AT PACHUCA BY THE EMPIRICAL METHOD.

The Pachuca mining district is over 400 years old; mining has proceeded with few interruptions throughout this long period, at once place or another within the district. Discovery and exploitation of ore bodies took place sporadically, and on a scale that looks small to modern eyes, until the first decade of the present century, when most of the district was acquired by powerful, progressive, foreign mining companies. The patio process was replaced by the cyanide process and the mines put in shape, with the aid of modern machinery and methods, to produce on a scale undreamed of by former operators. The result was a stepping-up, not only of production but necessarily also of discoveries.

Throughout the entire history of the camp, up to the present day, the ore bodies found have been discovered by use of the empirical method of exploration by penetrating settings which seem to resemble other settings known to contain ore.

Important outcrops of silver ore in the Pachuca district were limited to two small areas, one, the "discovery area" in the deep canyon north of the City of Pachuca, the other in northern Real del Monte (Figs. 1, 4). Not only were ore outcrops scarce, but outcrops of the veins themselves are in many areas inconspicuous or lacking. The premineral rock of the district appears as a window in the postmineral cover, as shown in Figure 1. The cover shown consists of alluvium, talus, recent basalt, etc. The outcrops of veins around the fringes of the mineralized area are naturally masked by the cover. But within the window of premineral rocks itself, many veins, strong and productive at depth, show feeble outcrops, and some show none at all, the vein-fracture wedging out upward, and ending far below the present surface (see pp. 468, 470, 475).

The result has been that mining in the district was restricted for centuries to the neighborhood of the two areas mentioned. The initial discoveries there doubtless were made because Spanish miners recognized oxidized silver ore (coloradas). In the area north of Pachuca (Fig. 1) the original discovery was

apparently made upon the Analcos vein outcrop where erosion had cut down into the ore bodies. The Analcos outcrop shows banded productive quartz and rhodonite; nearby veins such as the Maravillas carry identically similar gangue, and their high-lying ore shoots were soon found despite the fact that their outcrops were barren. In this area productive quartz, rhodonite, furnished empirical mineralogical ore guides that pointed to ore not far below them. The pitfall of empiricism in ore search is the fact that it relies solely on known ore environments and attempts to find their twins. To the early miners, productive quartz and rhodonite meant ore; therefore, veins or fractures lacking these minerals could carry no ore.

The result was that mining in the neighborhood of Pachuca was restricted to the area described until, in 100 years or so, all ore within it was exhausted, whereupon mining ceased in this part of the district, not to be revived until the middle of the 19th century.

The eastward extension of the Analcos vein is the Rosario (Fig. 1) which crops out as a well-defined fault almost completely barren of mineralization. About 1857, exploration at depth eastward from the old Analcos workings disclosed the Rosario bonanza. Empiricism had found something new: that ore might lie in a vein beneath a barren outcrop. At once other barren outcrops acquired interest; but empiricism demanded, with justice, that exploration be confined to those fractures having attitudes similar to that of the Rosario, i.e., an east-west strike and a southerly dip.

The major example of this fracture system in the Pachuca area is the Vizcaina (Fig. 1). Although the Vizcaina changes dip from southerly to northerly near its western termination, it carried the greatest bonanza in the entire district where it dips south. The Vizcaina outcrop, some 200 m above the top of the great ore body, is a broad zone of iron-stained altered rock, with sparse, tiny, quartz stringers. Although the elevation of the outcrop is no higher than that of the Maravillas (Fig. 2, north-south Section through Pachuca ore-belt) the "ore horizon"[3] dips north rather steeply here, which accounts for the great depth of ore beneath the present surface. In 1870, or thereabouts, a crosscut driven north, at the proper horizon, from the Maravillas area finally disclosed the Vizcaina bonanza.

The armory of empiricism by now contained four weapons: (1) knowledge that productive veins mainly had an east-west strike and a southerly dip; (2) the conception of an ore horizon with relatively gentle undulations, so that a crosscut driven at the optimum ore horizon on one vein might cut a nearby vein in ore; (3) that within and near the ore horizon productive veins show productive quartz, rhodonite and other mineralogical short-range ore guides; (4) knowledge that, provided the surface was far enough above the top of the ore horizon, productive quartz, etc. need not be demanded and a barren outcrop might overlie ore.

Competent geological work in the Pachuca district dates from about 1920 and still continues. Mapping and correlating rock formations added, for this

[3] By "ore horizon" is meant a gently undulating block of ground extending throughout the district, the top surface of which is developed by the tops of the ore bodies, the bottom surface, by their bottoms. Figure 4 shows structural contours taken on the top surface.

Pachuca area, a fifth empirical weapon: knowledge of the fact that the east-west, south-dipping fractures that carry most major ore bodies in the area are "normal" faults of measurable displacement. Conversely, all premineral "normal" faults with this attitude carry ore bodies (Fig. 2, north-south section through Pachuca ore-belt). During the writer's time at Pachuca the Alamo ore body (Fig. 1) was found, partly by this empirical guide.

Correlation of the rock formations provided also a sixth empirical ore guide: that ore shoots in the immediate Pachuca area were found along the east-west,

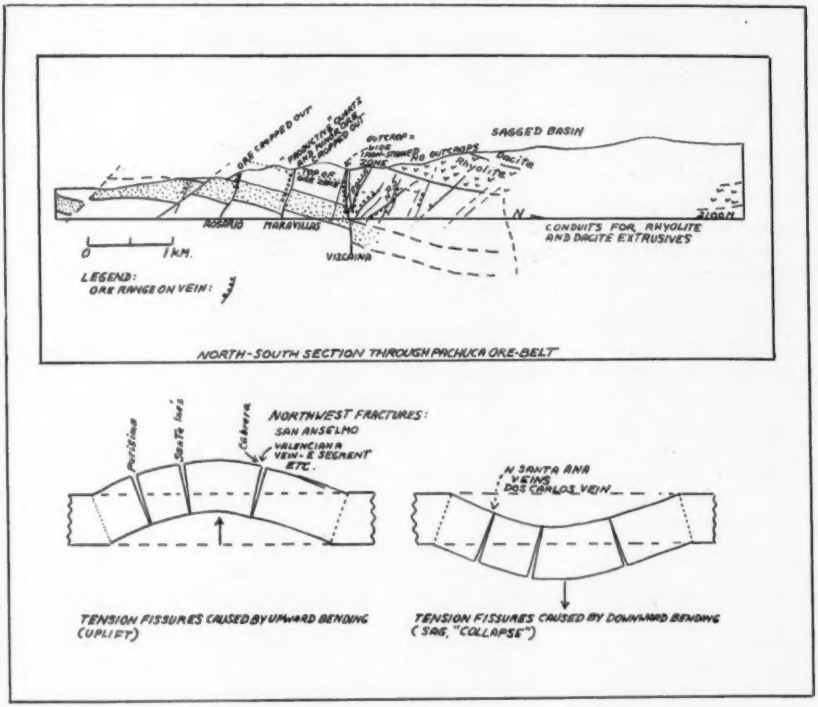

FIG. 2. Tension fissures caused by uplift and by sag; Pachuca tension fissures.

south-dipping "normal" faults only where both walls were the brittle, competent Pachuca andesite, a formational unit about 300 m thick. Since mapping showed that the Pachuca andesite had been eroded from the alluvium-covered valley south of Pachuca, that area was rejected for many years, until tectonic analysis suggested that a lower formation, also competent, might serve as a host rock for ore equally well, whereupon discovery of the Alamo, Tula, Arras, and Paricutin veins followed in quick succession. This illustrates the limitations and danger of empiricism.

Other empirical ore guides were used elsewhere in the district. The principle of empiricism has governed, in the main, exploration in the district from the first ore discovery to the present. Most recent discoveries have been of blind veins with no or scanty surface showings. Many such veins have been found by crosscutting gaps in evenly-spaced fracture patterns (Fig. 1: Purísima, Colón veins in Real del Monte; No. 5 and parallel veins, Santa Ana).

The empirical method of ore search is expensive and treacherous. Is there a better method, one that might be applied from the start of exploration of a virgin district thought to contain ore?

TECTONIC HISTORY OF THE PACHUCA DISTRICT.

The primary object of this paper is to evaluate tectonic analysis as a tool in the exploration of virgin districts. Underground workings in the Pachuca district are exceptionally extensive and they crisscross the mineralized area, in the shape of long haulage crosscuts, counterdrifts, etc., to an exceptional degree. Sound geologists have utilized these favorable opportunities to the full for the past 30 years. Pachuca structure, therefore, and the tectonic history behind it, are uncommonly clear. By setting forth first the known tectonic history of Pachuca, deciphered over many years, with the enormous help of extensive underground workings including hundreds of long drill-holes, a "control" is established whereby the merits of tectonic analysis based on surface data only, as would be the case with exploration of a virgin district, may be evaluated. In exactly the same way geophysicists test anomalies over a known ore body before trying their methods in unknown country.

Method of Analysis.—That portion of the tectonic history of a mining district that bears on the problem of ore localization is deciphered, by whatever data might be at hand. At Pachuca, unconformities between the extrusive formations, dikes of various generations and other features supply ample data for construction of a chronology of tectonic, extrusive and intrusive events, and the time relations of mineralization to these events (3, 5, 6, 7).

The development of the Pachuca fracture system has been described in general terms. Structural contour maps, the contours, showing elevations above sea-level, drawn upon the tops or bottoms of certain flows or tuff-beds have suggested that many fractures originated contemporaneously with folds in the extrusives, that they are localized upon such folds and that they owe their origin to stresses, mainly tensional, produced in the volcanics by the folding.

Two unconformities within the extrusive section offer evidence for three distinct periods of folding and fracturing. The lower unconformity is marked by a remarkably persistent water-laid tuff, averaging about 15 m in thickness, and found about half-way up the stratigraphic section. Beneath this tuff the extrusives are markedly folded and fractured in many places. After what may be called the First period of deformation, the region was peneplained and the tuff laid down in a large lake, or series of contiguous lakes.

The tuff itself, however, and the thick series of andesitic flows poured out on top of it are strongly folded in places, this folding marking the Second period of deformation. Fractures accompanied this folding also.

Finally, the rhyolites and overlying dacites were extruded with unconformity upon the surface of the older rocks. The surface was one of high relief, so that in places the extrusions show strong initial dips; but tectonic warping during and after extrusion took place in several areas. The warping was accompanied by fracturing genetically related to the basins, domes, and "anticlines" produced. This is the Third period of deformation.

To decipher the tectonic history involved in these three deformation periods, the effects of each period must be successively disentangled from the structure as seen today, which reflects effects of all three periods. Present structure portrays faithfully effects of the Third deformation period. But to see what the region looked like at the end of the Second period, the bumps and basins of the Third period must be "flattened out" and fault movements belonging to the Third period reversed, the fault blocks being restored to their pre-faulting positions.

In the same way, portrayal of results of the First period demands restoration of the tuff bed to its former horizontal position and a nullification of the effects of faulting that took place during the Second period.

The evidence of successive generations of dikes, of successive stages of hydrothermal alteration, and of successive stages of mineralization serves as a check on the time relations of fracturing deduced from the tectonic analysis.

First Period of Deformation.—This was marked chiefly by formation of a major northwest anticline, the axis of which lay southwest of the southwest corner of Figure 1. The area shown in that figure lay, therefore, on the northeast flank of the anticline.

The anticline was not produced by tangential compressive stress, but by local, vertical force that arched up the brittle plate of volcanics. This is shown by the fact that the northeast flank of the anticline is broken by a closely-spaced system of longitudinal tension fissures and faults, striking northwest, parallel to the anticlinal axis, and dipping southwest, toward the core of the anticline. These fractures were formed in response to arching and consequent stretching of the plate, as suggested diagrammatically in Figure 2, lower left-hand sketch. In Figure 1, only the members of this system that contain ore bodies are shown, such as the Encino, Corteza and others in the Pachuca area, and the Eduardo and Gran Compaña in Real del Monte. The Vizcaina vein-fracture appears to be the major representative of this system.

As suggested in the lower left-hand sketch of Figure 2, tension fissures formed by arching of a brittle plate tend to narrow downward.

The Santa Gertrudis and Dos Carlos vein-fractures (Fig. 1) belong also to this early period. They lie along the curving southern rim of a basin sinking at this time ("Pre-Rhyolite Basin," Fig. 1). Like the northwest fractures they originated as tension fissures caused by local stretching of the brittle plate of extrusives; but the plate in their case was stretched by sag instead of uplift. In a region of such active magma movements as Pachuca, sag basins caused by removal of magma from below, as well as anticlines caused by upward movement of magma, are to be expected; and indeed positive evidence is at hand for the magmatic origin of the "Intra-Rhyolite Basin" shown in Figure 1 (p. 470).

As shown in the lower right-hand sketch, Figure 2, tension fissures caused by downward bending tend to widen with depth, to wedge out upward.

Precise dating of this fracture system, shown by tectonic analysis to be the oldest in the district, is not possible on the evidence of dike generations, alteration and mineralization. But these fractures carry the oldest known dikes, which long antedate the mineralization; they are capped by rhyolite flows in places; they often show intense hydrothermal alteration and early vein minerals. Where not torn open by intramineral stress during the silver surge of mineralization they remained sealed by dikes or early vein-matter.

Although the vein-matter must have entered fractures of the northwest system long after the fractures formed, the cross-section of the veins conforms to the original shape of the fissure: such veins are widest at the surface and narrow downward. The Dos Carlos vein also must have formed long after the Dos Carlos fracture; but the vein wedges out upward, far below the present surface, and is one of the veins, mentioned above, that has no outcrop although its position on the surface, projected up the dip, falls in an area where no post-mineral cover exists.

Second Period of Deformation.—The tuff-bed marking peneplaination after the close of the First period has been eroded from much of the district, together with the andesitic extrusives above it, so that information regarding the Second period of deformation is fragmentary. Recurrence of sag north of Santa Gertrudis restored the Pre-Rhyolite Basin, in somewhat different form; the Santa Gertrudis and Dos Carlos fractures probably developed further at this time, working their way upward to some extent through the younger rocks above the tuff.

In northern Real del Monte a minor north-south anticline appeared. The Purísima and Santa Inés vein-fractures north of the Gran Compaña fault, and the Cabrera vein-fracture (Fig. 1), originated during this folding as tension fissures on either slope of the anticline. Each dips toward the anticlinal axis as suggested in Figure 2, lower left-hand sketch. These fractures later became loci for the earliest veins, which are widest at the surface and narrow with depth, as do the veins in northwest fractures of the earlier period.

Third Period of Deformation.—This period was essentially contemporaneous with the hydrothermal alteration and mineralization. There was an extensive time-gap between the First and Second deformation periods, evidenced by peneplaination of the district; but the interval between the Second and Third periods seems to have been short. No peneplaination separates the two periods; extrusion of the rhyolites, which marked the opening phase of the Third period, took place in part upon a plateau-like surface with steep sides, not unlike the present configuration of the Sierra de Pachuca. It is difficult to separate present-day warpings of the rhyolite flows and tuffs into those due to irregularities in the surface upon which these formations were laid down on the one hand, and those due to tectonic activity during and after the extrusion, on the other.

Figure 4 shows structural contours taken on the base of the rhyolite series. In the southern part of the district the rhyolites descend into a broad basin. Although rhyolite necks exist in this basin, obviously the source of the rhyolite flows there, this basin may not be due to sag attendant on transfer of magma

from below to the surface, but may well have existed at the time of rhyolite extrusion, with the central part of the district an east-west plateau as suggested by the structural contours.

If so, the chief vents for rhyolite extrusion lay upon this plateau, one east of the area of Figure 1 and Figure 4, the other near the central portion of the Intra-Rhyolite Basin shown in the northwest corner of the figures, slightly north of the north edge of the maps.

Mineralization started, probably just after extrusion of the rhyolites and during extrusion of the overlying dacites. Hydrothermal alteration of fracture walls was effected along many pre-mineral fractures, including members of the old northwest system and the Purísima, Santa Inés, and Cabrera vein-fractures in Real del Monte north of the Gran Compaña fault. Activity of altering solutions persisted through the time of formation of some of the earlier intramineral vein-fractures to be described, evidenced by alteration of their walls.

Vein formation appears to have started in the northern Real del Monte area described (3). The Purísima, Santa Inés, and Cabrera veins here contain mainly the early vein minerals, gray quartz, massive pyrite, dark sphalerite. Veins in this area, except the Cabrera, carry only sporadic ore, and evidence for the tearing open of early vein matter to admit later silver ore and productive quartz is conclusive. As stated above, these northern veins are widest at the surface and narrow downward, conforming to the shape of the premineral fissures that contain them.

Shortly after formation of these early northern veins, shearing stress operative in a plane nearly horizontal became active in Real del Monte. The mechanics of this shearing deformation form the main thesis of the writer's first paper on Pachuca (3); repetition of the thesis is beyond the scope of the present paper. Under the influence of this shearing stress the ground in Real del Monte tended to flow toward the west. The flow is now thought to have been drag above a body of magma moving westward at depth, possibly the dacite magma moving toward the rhyolite-dacite vent north of the Pachuca area (Intra-Rhyolite Basin). The vein-fractures mentioned in northern Real del Monte were so oriented as to serve as strike-slip antithetic faults assisting this flow, in the manner described in the 1937 reference. Seizing on these pre-existing north-south fractures, shearing stress propagated them southward just as the silver surge of metallization appeared, so that by the time they had reached the area south of the Gran Compaña fault they caught the localized bonanza ore bodies (Fig. 1). These ore bodies carried a gangue of productive quartz only, with light brown sphalerite and galena; the vein walls here are notably devoid of strong hydrothermal alteration.

It was the horizontal shearing stress that reopened the older, northern veins which had been sealed by early vein matter; these veins were reopened only where their attitude most closely approximated that of the intramineral vein-fractures to the south (Cabrera vein, Fig. 1).

It follows that older veins filled with early vein matter and carrying only sporadic ore show much more gangue than ore upon a vertical longitudinal projection, whereas vein-fractures forming only during the time of the silver-pro-

ductive quartz surge show gangue practically coextensive with ore, within the ore horizon.

Furthermore, while the older northern veins, originally tension fissures narrowing downward, are widest at the surface and narrow with depth, the younger southern vein-fractures, generated by a stress at depth and dying out upward, strengthen downward and wedge out upward, as do the veins that fill them.

Figure 3 is a vertical longitudinal projection of the Santa Inés vein, showing its older segment, north of the Gran Compaña fault, and its younger segment south of that fault. While gangue is sporadic in the northern segment, there is far more gangue than ore, and the gangue bodies are widest at the surface, narrowing downward. The southern segment, where the vein-fracture formed only in time to catch the rich surge of metallization, shows, within the depth limits of silver deposition, gangue roughly coextensive with ore. Below the silver ore deep drilling shows that quartz, with base sulphides, continues strongly down the dip. The silver ore body lies at the tip of a great tongue of quartz sticking up from below.

The southern, younger segment of the Santa Inés narrows nearly to a knife-edge at the surface and widens with depth, a striking example of tectonic ore control.

The north-south vein-fractures in Real del Monte were working south and catching ore while the dacite was extruding, largely from the volcanic center north of Pachuca. Here the transfer of immense masses of rhyolite and dacite from the depths to the surface created a large sag basin centering around the conduits through which the magma reached the surface (Fig. 2, north-south section through Pachuca ore-belt). Along the southern rim of this sagging basin tension fissures formed in the same manner as did the Santa Gertrudis and Dos Carlos fissures at an earlier period. (Falla, No. 5 and parallel fractures shown in Figure 2.) Since these fractures formed at the time of the silver surge their gangue is roughly coextensive with ore. Since they formed by downward sagging of a brittle plate, they taper upward to a knife-edge as does the Dos Carlos vein-fracture, their earlier counterpart.

The Vizcaina vein-fracture, the major fracture of the district, probably started as a longitudinal tension fissure along the northeast flank of the major anticline of the First period of deformation. The nature of the displacements on this fault is significant. Except for its west end, it dips south throughout its course. In Real del Monte it is a "normal" fault, the south or hanging wall having dropped with respect to the footwall. The south wall probably actually dropped in space, because the Pre-Rhyolite sag basin lay on the south side of the Vizcaina, not only in the First period of deformation, but also during the Second. The downward pull which caused the basin would naturally take advantage of the existing Vizcaina fracture.

At about midpoint on the Vizcaina (Coördinate 1700E, Fig. 1) displacement on the Vizcaina is nil; but west of here, opposite the Intra-Rhyolite sag basin, the north wall of the Vizcaina dropped with respect to the south wall, and probably also actually, for the Intra-Rhyolite sag to the north would utilize the Vizcaina as did the Pre-Rhyolite sag (north-south section through Pachuca ore-belt, Fig. 2).

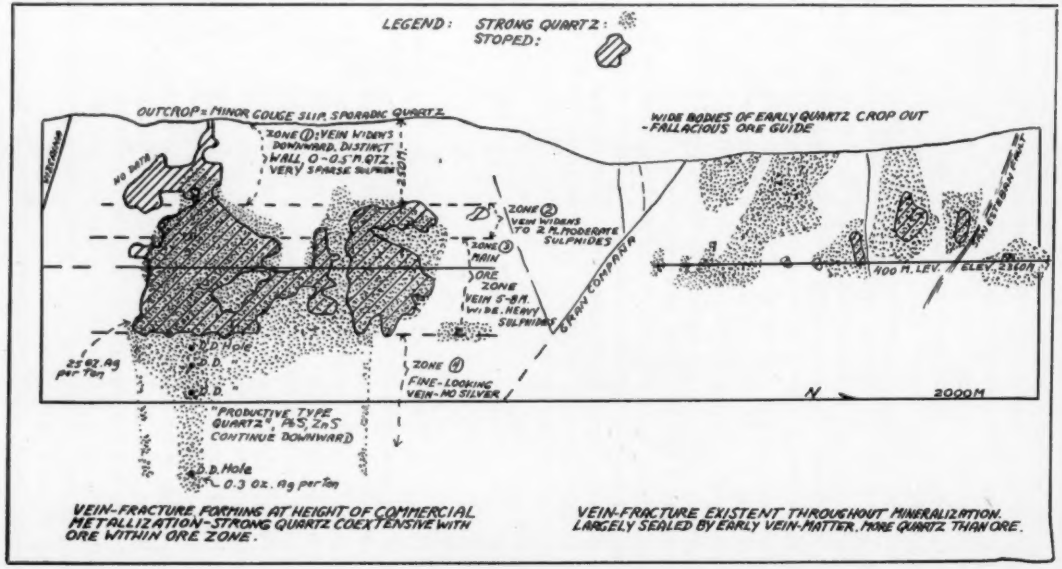
LEGEND: STRONG QUARTZ:
STOPED:
OUTCROP = MINOR GOUGE SLIP, SPORADIC QUARTZ
WIDE BODIES OF EARLY QUARTZ CROP OUT
-FALLACIOUS ORE GUIDE
ZONE ①: VEIN WIDENS DOWNWARD, DISTINCT WALL, 0-0.5 M QTZ. VERY SPARSE SULPHIDES
NO DATA
ZONE ②: VEIN WIDENS TO 2 M. MODERATE SULPHIDES
ZONE ③ MAIN ORE ZONE: VEIN 5-8 M. WIDE. HEAVY SULPHIDES
CERRO COMPANA
400 M. LEV.
ELEV. 2160 M.
N
2000 M
D.D. Hole
25 OZ. Ag per Ton
ZONE ④: FINE-LOOKING VEIN-NO SILVER
"PRODUCTIVE TYPE QUARTZ", PbS, ZnS CONTINUE DOWNWARD
D.D. Hole
0.3 Oz. Ag per Ton
VEIN-FRACTURE FORMING AT HEIGHT OF COMMERCIAL METALLIZATION-STRONG QUARTZ COEXTENSIVE WITH ORE WITHIN ORE ZONE.
VEIN-FRACTURE EXISTENT THROUGHOUT MINERALIZATION. LARGELY SEALED BY EARLY VEIN-MATTER. MORE QUARTZ THAN ORE.

FIG. 3. Vertical longitudinal projection of Santa Inés vein, Real del Monte.

The Pachuca ore-belt (Fig. 1) trends west of north, its axis heading straight for the Intra-Rhyolite basin. The suggestion is that of strong tensional pull exerted by the sag, and extending far south of the basin. However, the Maravillas, Rosario and other veins south of the Vizcaina dip more steeply than do the obvious sag veins north of the Vizcaina (Falla, No. 5 etc. shown in Fig. 2) and they maintain more constant width with depth. They probably formed in a hinge zone between the sagging basin to the north and an uplift on the south as suggested in the Section of Figure 2.. If these hinge zone fractures owe their origin both to down-bending of a brittle plate and to up-bending of the same plate, the tendency of the one stress to make the fissures narrow upward would be counteracted by that of the other stress to make the fissures widen upward, and the veins within these fissures would maintain constant width.

Figure 1 shows several of these intramineral vein-fractures linking up with fractures of the old northwest system, as the Maravillas with the Encino and the Analcos with the San Anselmo. These older fractures, while not well oriented to respond to the intramineral tensional stress, and often sealed likewise with dikes and early vein-matter, were nevertheless reopened in this highly dynamic area at the time of entry of the silver solutions.

The Santa Gertrudis and Dos Carlos fractures, dating from the First period of deformation but probably revived in the Second period, were inert at the start of mineralization during the Third period. Mineralization started, as has been said, in northern Real del Monte, and proceeded southward, keeping step with the tectonic activity developing in that direction. The southward march of tectonic activity and mineralization eventually reached the Santa Gertrudis-Dos Carlos area. Horizontal stress opened these old fractures just in time to receive bonanza ore shoots.

THE PACHUCA ORE HORIZON.

Mention of the most valuable empirical ore guide in the district has been delayed until the structure and tectonic history could be outlined. Figure 4 shows the remarkable concordance between the bottom surface of the rhyolite extrusives (a surface that reflects both the relief of the sub-rhyolite surface and tectonic warping of the rhyolites) and the imaginary surface developed by drawing contours through the tops of the ore bodies (top surface of the "ore horizon"). The two surfaces together give an uncanny picture of the surface existent at the time of metallization, because since the dacites are in general conformable above the rhyolites, the actual surface of the ground probably conformed closely to that of the base of the rhyolites. Ore bodies topped at a depth from 300 to 500 m below the base of the rhyolites. Despite the variation in depth from rhyolite to top of ore, the *shape* of the rhyolite surface, on the one hand, and that of the ore horizon surface on the other are remarkably similar. Credit for this discovery belongs to C. D. Hulin, who suggested making the map, shown by Figure 4, to the writer.

This ore guide proved of value in selecting horizons for lateral exploration. The ore horizon, although a consistent "blanket," nevertheless has major undulations so that the proper horizon for exploration in one area may differ by hundreds of meters from that in a distant area.

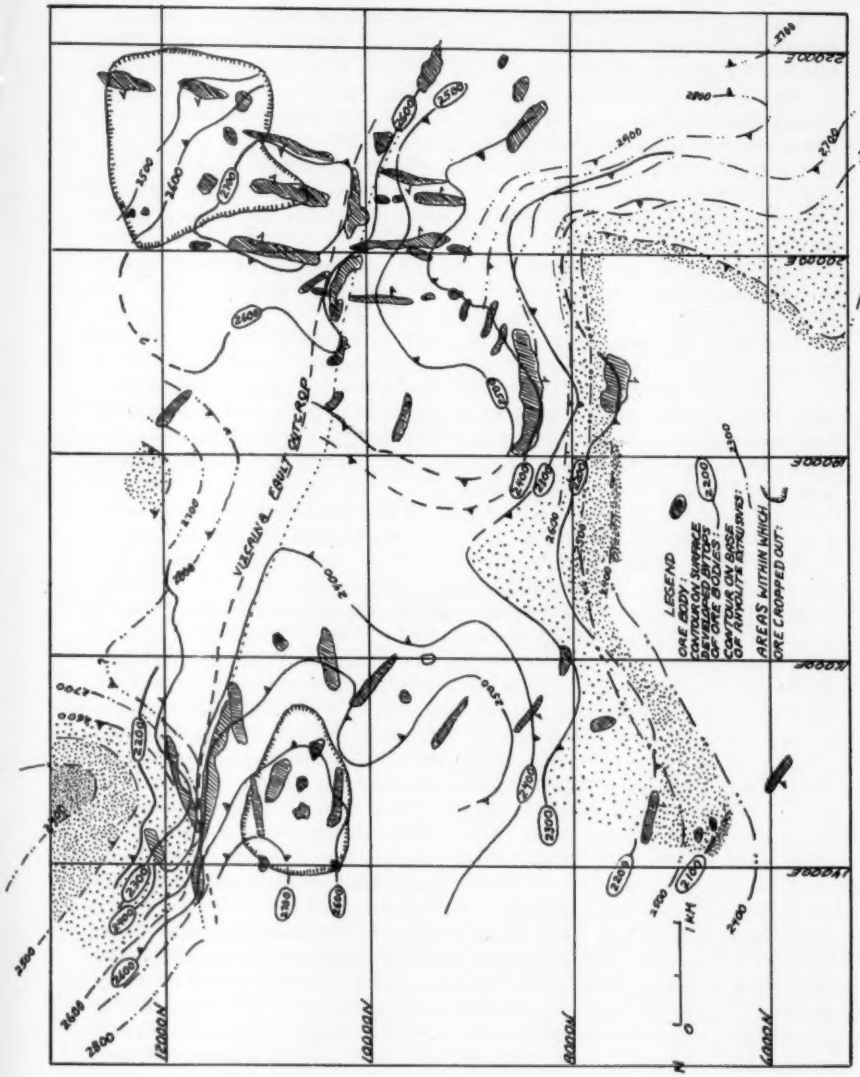

FIG. 4. Structural contours on surface developed by tops of ore bodies, and on bottom surface of rhyolite extrusives.

TECTONIC ANALYSIS AS A TOOL FOR PACHUCA EXPLORATION.

Knowing the essentials of Pachuca structure, tectonic history and metallization, it is of interest to speculate on how valuable tectonic analysis would have been had its principles been applied when the district was virgin.

How useful tectonic analysis might have been depends on how much of the critical evidence could be gathered at the surface. The entire rock section, with evidence for the unconformities, and the essentials of the structure may be seen on the surface. The history of the critical period may largely be read in daylight. The time relations of mineralization to deformation, intrusion, and extrusion may, to a considerable extent, be determined. The key to the problem was, therefore, at hand.

From the standpoint of exploration for ore, the showings of mineralization visible on the surface, interpreted in the light of tectonic analysis, might have produced the following ore guides.

Northwest Fracture System.—Time relations of the various dike generations, of the early vein-matter and of the younger, silver-bearing vein-matter are manifest on the surface. Within the areas where ore cropped out the productive quartz would be recognized, as well as the earlier barren quartz on northwest fractures within these areas, such as the Encino vein (Fig. 1). Strong hydrothermal alteration along fractures bearing largely early quartz would be discounted as a guide to ore.

Regional structural studies would have revealed the origin of the northwest fractures as longitudinal tension fissures along the flank of an anticline, and the corollary that the veins of this system "put their best feet forward," that is, that the quartz bodies are widest at the surface and taper downward. It would be suspected that a narrow vein outcrop (and these veins are typically narrow) would be likely to pinch still farther in depth.

North-South Veins of Northern Real del Monte.—On the surface these early veins seem to stop abruptly on the south. It is now known that this is because they change their nature from north to south (p. 470), from veins widest at the surface to veins narrowest toward the surface. The Santa Inés vein cropped out just south of the Gran Compañía fault, as a narrow quartz stringer along a well-defined wall. While sinking to moderate depth on this stringer would have shown the habit of this vein class to widen with depth, it is doubtful whether surface exposures would have disclosed the mode of formation of the north-south vein-fractures of central and southern Real del Monte (3).

Santa Gertrudis and Dos Carlos Veins.—Surface mapping would have shown the existence and early age of the Pre-Rhyolite basin (Fig. 1). The southerly dip and curving strike of the Santa Gertrudis fracture, paralleling the contours of the south slope of the basin, might have offered a hint on the genetic connection of fracture and basin. Since the Santa Gertrudis would be recognized as an early fracture, long antedating the mineralization, some cause for its activation at the time of metallization would be sought. That it was so activated would become clear as the Santa Gertrudis, which shows productive quartz in its outcrop, was explored at depth, because the productive quartz sticks close to ore, indicating a vein-fracture opening only in time for the silver surge of metallization.

Actually the Santa Gertrudis and Dos Carlos old fractures were opened by horizontal shearing stress identical in nature with that which formed the north-south vein-fractures in central and southern Real del Monte (3). The visible signs of this stress in the Santa Gertrudis area are southwest intramineral strike-faults transecting the Santa Gertrudis and Dos Carlos fractures at acute angles; movement on these faults tended to open the old fractures to receive ore bodies. But these faults have no outcrops. It is therefore unlikely that reasons for ore localization on the Santa Gertrudis vein-fracture could have been determined without extensive underground work. Once the cross-section, tapering upward, of the Santa Gertrudis had been ascertained, the genetic connection of that fracture with the Pre-Rhyolite basin would have been verified and crosscuts north and south would have been in order in the hope of finding a parallel sag fracture that might have wedged out before it reached the surface. Such work would have found the Dos Carlos vein by tectonic analysis, and not by blind crosscutting based on empiricism, the way that vein actually was found.

Pachuca Area.—The east-west veins south of the Vizcaina, where ore cropped out, would have explored themselves. Virgin bonanzas however lay north of the Vizcaina, and on the Vizcaina itself. They had no or poor outcrops to indicate them. The probability that the Intra-Rhyolite basin sank during the period of mineralization would have been brought to light in the course of the tectonic analysis. The known relation of the Santa Gertrudis vein, with a strong quartz outcrop, to the basin north of it might lead a bold explorer to seek similar veins on the south side of this Pachuca basin despite the absence of strong outcrops there. The notable Vizcaina fracture, with its attitude in the Pachuca area conforming to that of a sag fissure related to the basin, and its outcrop, although poor, at least a wide, persistent zone of hydrothermal alteration with a little quartz might have made a fairly attractive initial target for a crosscut pointed north from the known ore-bearing area. Once the Vizcaina bonanza had been discovered and its upper and lower limits defined, a crosscut driven north at a horizon cutting the heart of the Vizcaina bonanza would have speared in succession all of the Santa Ana sag veins. If the crosscut had been run too high and cut these veins where they show merely as slips with minor mineralization, knowledge that sag veins widen downward would have indicated the need for exploration of these stringers at depth. With a crosscut at too low a horizon, a wide, diffuse, barren vein would suggest ore at higher levels, for with vein-fractures that wedge out upward, ore tends to localize from the point of the wedge downward.

The chief fruit of tectonic analysis of the Pachuca district, had that exploration tool been applied from the start, would have been design of exploration campaigns in places well away from known ore and from outcrops of productive quartz. Successful development of the method would eventually have led to the search for blind veins; but before that stage, veins with narrow or otherwise unpromising outcrops would have been explored, where study of the tectonics offered promise that such veins would widen with depth. Here a major problem in the exploration of vein districts is involved.

Exploration of Veins with Narrow Outcrops.—Veins that widen upward put their best feet forward, as has been said. The prospector sees such veins

at their best and soon tests their possibilities for ore. But veins that widen downward and narrow upward present a problem. Mineralized districts commonly abound in stringers and barren slips. They cannot all be explored. How can the small showings that represent the tops of great veins be picked out of such a swarm?

The answer, at Pachuca at least, lies in the fracture and fault pattern. The Santa Ana productive sag veins show an even spacing in plan; they are persistent, especially along the strike, and are mainly normal faults, of slight but measurable displacement. Many parallel fractures exist in the blocks between the ore-bearing veins; some of these are persistent faults. But the rule of spacing holds: such fractures are barren.

South of the Vizcaina the east-west veins are more important faults which also show consistent spacing (Figs. 1, 2). Here the rule of spacing is reinforced by the rule that only important faults carry important ore.

In Real del Monte the productive north-south veins show regular spacing; as has been said, several of these were found by crosscutting gaps in the fracture pattern.

CONCLUSION.

Speculation such as the above concerning what tectonic analysis might have accomplished had it been used from the start at Pachuca is infected with hindsight. Nevertheless the possibilities of this exploration tool seem exciting and worth testing.

The main object of the paper, accordingly, has been less to describe the tectonic history at Pachuca and the guides to ore it suggests, than to demonstrate the possibilities of tectonic analysis in the exploration of virgin districts. Pachuca, where tectonic control of ore localization is well established, has been used merely to test the validity of tectonic analysis as that method might have been applied when the district was virgin.

The use of such a method demands expenditure of time and money on a scale seldom thought warranted in exploration of unproved mining districts. Regional study would have to be extended perhaps many miles away from the showings that aroused initial interest in the district. Districts might be considered worthy of exploration on the basis of structure and tectonic history alone, despite the fact they show next to no mineralization.

Such exploration will entail high risk; but it is generally agreed that future mining exploration in the United States must be venturesome, if ore districts lying within minable reach but as yet undiscovered are to be found. If tectonic analysis proves to be a principal key to the riddle of why ore is where it is, then the chief objective of the regional studies mentioned will be to unravel the sequence of events, dominated by tectonics, that took place in the critical period which, in a productive ore district, culminated in metallization.

ACKNOWLEDGMENTS.

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UNIVERSITY OF CALIFORNIA,
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March 28, 1951.

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THE AGE OF THE GRANITES OF THE NORTHERN RHODESIAN COPPERBELT.

W. G. GARLICK AND J. J. BRUMMER.

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ABSTRACT.

The writers maintain that no Younger Granite has been observed on the Copperbelt. They quote the various references describing this supposed granite and show that on three of the mines, underground development, additional surface work and diamond drilling have proved that all the so-called Younger Granites are merely variations of the Old Granite. They date the Old Granite to be post-Lufubu System and probably pre-Muva System.

INTRODUCTION.

THE age of the granite in the Northern Rhodesian Copperbelt has been a much debated problem and one of considerable importance in determining the origin of the mineralization of these ore deposits. Most of the earlier geologists recognized at least two types of granites which have been called by various names and, for the sake of simplicity, will here be referred to as the "Older" and "Younger" granites. The prefixes "Older" and "Younger" are relative terms and refer to granites which are older or younger than the sediments of the Katanga System which contain the economic copper deposits. The mineralization has, in the past, usually been attributed to the intrusion of the Younger Granite into the lowermost beds of the Katanga System, known as the Roan sediments, and the hydrothermal solutions which were given off by this cooling mass of granite then travelled along certain favorable horizons which they mineralized.

The necessity for finding a magmatic source for the hydrothermal solutions believed to be the cause of the copper deposits was probably a cogent reason for rather hastily accepting the meagre field evidence as proving a Younger Granite. It must be remembered that similar evidence was accumulating at the other prospects and developing mines on the Copperbelt and the unanimity of the geologists appeared to be overwhelming. The dissenting voices were few, namely Dr. Anton Gray, Professor J. W. Gregory and Dr. H. Schneiderhöhn, and only the latter stated his views emphatically in print.

If all the so-called "Younger" Granites can be shown to be simply varieties of the Older Granites then the question of the origin of the deposits must be re-examined.

The authors are attempting only to establish the fact that there are no Younger Granites in the Copperbelt and their remarks do not apply to areas outside it. Younger intrusives of acid composition do exist elsewhere in Northern Rhodesia, especially in the Lusaka district, and are not discussed in this paper. Furthermore, the authors do not claim to be the first to realize that the evidence for the so-called Younger Granites is inadequate. Credit must be given to H. Schneiderhöhn [1] for this observation. He stated in 1932 that he did not agree with the Copperbelt geologists after examining their evidence. The senior author re-opened the problem in 1940.

GENERAL GEOLOGY.

Before proceeding further, it is desirable to outline briefly the general geology and stratigraphy of the Copperbelt.

Most of the area is underlain by an extensive mass of granite, deeply eroded and containing roof pendants of highly metamorphosed Basement schists, some of which have been intruded by this granite. Resting unconformably on these are synclinal remnants of less metamorphosed sediments known as the Katanga System. The Basement sediments are locally known as the Lufubu and Muva Systems and consist of schists and recrystallized quartzites.

The sediments of the Katanga System consist of conglomerates, arkoses, felspathic quartzites, shales, argillaceous quartzites and dolomites. These sediments have been strongly folded into a series of synclines and anticlines.

The age of the Basement Systems is Archaean and the Katanga System is considered to be late Precambrian.

The economic copper mineralization occurs in a shale, argillite, graywacke or quartzite horizon, depending on its location, situated near the base of the Katanga System. It is, generally, very extensive and is remarkably regular in values and width. Figure 1 shows the location of the different mines on the Copperbelt.

As already stated, earlier geologists considered the granites to be of two different ages: the Older intrusive into the Basement schists and the Younger intrusive into the Katanga System.

[1] Schneiderhöhn, H., Mineralische Bodenschätze im südlichen Afrika, Nem-Verlag, Berlin. Translation and abstract in The Mining Magazine, April 1932.

FIG. 1. Map showing location of the different mines of the Copperbelt.

Stratigraphic Column as at 1931.

Katanga System	Kundelungu Series		Quartzites, shales, dolomites and tillites
	Mine Series	Mwashia Group	Sandstones and shales
		Upper Roan Group	Dolomites and shales
		Lower Roan Group	Shales, quartzites, arkoses and conglomerates
	Unconformity.		
Muva System			Schists and quartzites
	Unconformity.		
Lufubu System			Schists and gneisses

Younger Granite intrusive into Lufubu, Muva and Lower Roan Group.
Older Granite intrusive into Lufubu and Muva Systems.
Gabbro intrusive into Upper Roan Group.

EXTRACTS FROM PREVIOUS PUBLICATIONS.

As considerable data has been accumulating since 1931, the evidence for the Younger intrusive granite as stated in previous publications will now be reviewed in part as a basis for the re-examination of the problem.

The following extracts are, in chronological order, from past publications that have discussed the Younger Granites:

J. Austen Bancroft and R. A. Pelletier [2] state:

(5) *Younger Granite:* Intrusive into the Bwana Mkubwa Series (Roan Group) and older rocks are batholiths and numerous stocks of granite . . . in places somewhat gneissoid.

These granites, and especially their pegmatitic phases, occasionally contain a few scattered grains of chalcopyrite and pyrite. The ore bodies at Lunsemfwa and Mtuga occur chiefly as disseminated chalcopyrite in portions of bodies of the younger pink biotite-granite, with associated pegmatite and aplitic phases, that have there invaded the older Mkushi gneissoid granites.

Very numerous instances might be pointed out where altered sedimentary rocks within the radius of contact influence of these granites contain copper deposits. It is believed that it was during the advance and cooling down of these granites that mineralising solutions were liberated which led to the development of the important copper deposits of Northern Rhodesia.

The above description groups the Copperbelt deposits with those of Lunsemfwa and Mtuga [3]—a point with which the authors are not in agreement.

Again J. Austen Bancroft [4] states (p. 25): ". . . in some places these (Older Granites) were intruded by stocks, dykes and small irregular bodies of a younger granite. Moreover, the ore-bearing horizon at Nkana is traversed by a few narrow pegmatite dykes. Hence, when Shaft No. 1, at a depth of 225, passed from the basal felspathic sandstones of the Bwana Mkubwa series into a body of the younger granite, it was not surprising to find that an intrusive contact was exposed."

Again on p. 27, the above writer states: "It is believed that during the advance and cooling down of the younger granites and their associated pegmatites, mineralizing solutions emanated which, through processes of replacement, were responsible for the primary mineralization of the ore-bearing beds at Nkana."

D. C. Sharpstone [5] writes: "Post Roan granite probably occurs in at least two localities, both about 3½ miles west of the Luanshya, one on the North side of the Roan series, the other on the South side. In both instances, granite is believed to have cut out several hundred feet of the footwall of the Roan Series, and appears to have likewise cut out a portion of the copper-bearing horizon. . . . The intruded rocks are, in general, rather extensively metamorphosed. . . . Metamorphic aureoles are variable in width and incompletely known, but around a body of granite, believed to intrude the Roan Series, 3½

[2] Notes on the general geology of northern Rhodesia: International Geological Congress Guide Book, Excursion C.22, p. 9, 1929.

[3] Located 80 miles southeast of the Roan Antelope Copper Mines, Limited.

[4] Notes on the geology of the Nkana Mine. Same Guide Book.

[5] An outline of the geology and development of the Roan Antelope Mine. Privately published by R.A.C.M. Limited, p. 12, March 23rd, 1929.

miles west of Luanshya, it is between 150 ft. and 200 ft. wide. This contact aureole contains considerable quantities of intruded pegmatite." (Fig. 2.)

Four distinct types of dikes, according to Sharpstone, cut the Roan Series, of which the most important type is probably the pegmatite variety. He points out that there are pegmatitic noses, apophyses and dikes around granite contacts, and small pegmatite dikes distributed throughout the Roan Series, which are potash feldspar, quartz-pegmatite, and siderite-pegmatite dikes, the former being more abundant. The first contain peculiar magnesium-iron-bearing calcite, muscovite, plagioclase, specular hematite, bornite, chalcocite and rarely chalcopyrite.

Sharpstone further states (p. 28): "The mineralization is considered to be genetically related to the post-Roan granites and more particularly to the residual magmatic juices derived from it during its consolidation. The later products of granitic activity were clearly often rich in mineralizers and are rather extensively represented in the Roan Series as seams, ribbons and dikes of acid pegmatites. Many of these pegmatites carry copper in the form of bornite and chalcocite. . . ."

D. M. Davidson [6] states: "The granite at Chambishi . . . unquestionably intrudes the Roan sediments. At the base of the ore shale it appears to have been injected along a fault and is now an intrusion breccia containing fragments of both the ore shale and footwall quartzite. This breccia, as well as the main mass of granite, contains a little copper. . . . Garlick has suggested a sill-like method of intrusion for the granite for . . . the intrusive contact varies but a few degrees from the dip of the sediments. . . . To the writer, the source of the Chambishi ore is undoubtedly the magma which solidified into granite. The granite itself carried traces of copper, and pegmatites and quartz veins that come from it also carry copper sulfides. Also, the ore shoot shows a definite relationship in regard to proximity of granite. . . ."

Anton Gray [7] states (p. 318): "The rocks of the 'basement complex' and the overlying Katanga System . . . were intruded by large masses of granite, the 'younger grey granite.' This intrusion was accompanied by mineralization, and the copper deposits of the region were formed at this time. . . . The granite . . . has not penetrated far into the sediments, but the latter are highly silicified near the contact and contain numerous dikes of granite material as well as an unusual number of quartz veins. . . . This granite contains many small quartz-pyrite-chalcopyrite veins. . . ."

Jackson [8] distinguishes three varieties of "older" granites in the Nchanga district, the Muliashi porphyritic granite-gneiss, Nchanga older red granite, Mkushi granite-gneiss and two varieties of "younger" granites, *viz.*, younger grey granites and Nchanga younger red granite. He states (p. 455) that "Under the microscope there is no essential mineralogical difference between the typical Mkushi granite-gneiss and the younger grey 'granites'" and that (p. 483) "The relationship of the younger grey 'granite' to the Nchanga

[6] Geology and ore deposits of Chambishi, Northern Rhodesia: ECON. GEOL., vol. 26, March–April, 1931.

[7] The Mufulira Copper Deposit, Northern Rhodesia: ECON. GEOL., vol. 27, no. 4, June, 1932.

[8] Jackson, G. C. A., The geology of the Nchanga District, Northern Rhodesia: Geol. Soc. Quart. Jour., no. 351, 1932.

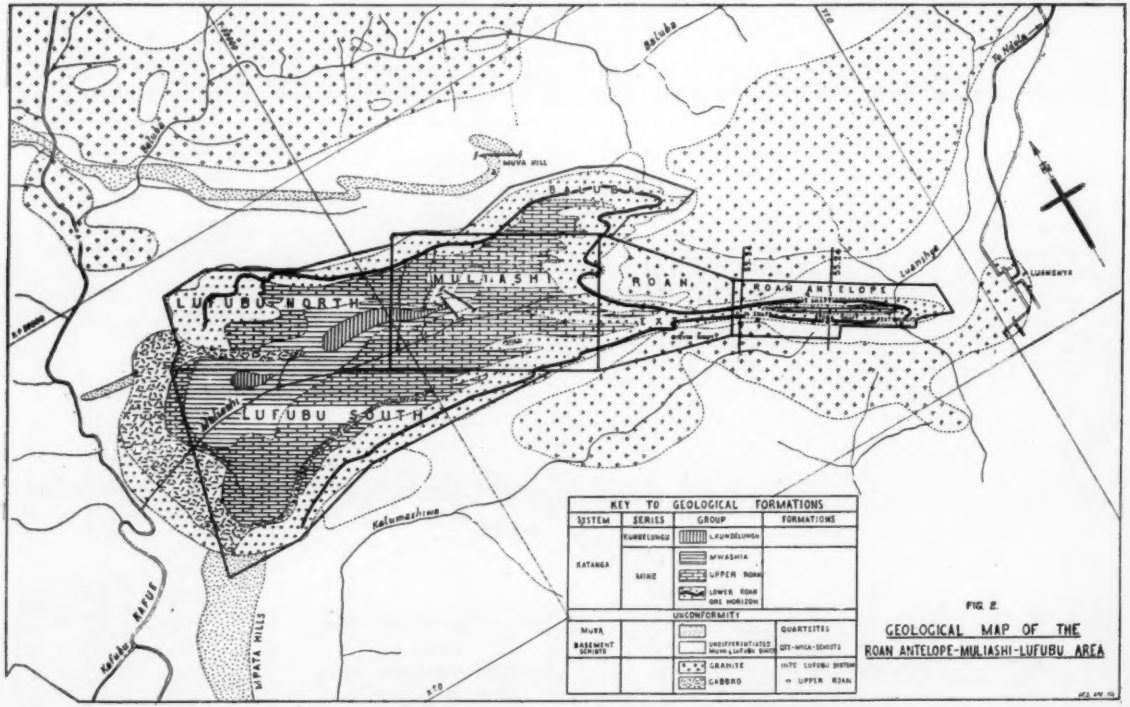

FIG. 2. Geological map of the Roan Antelope-Muliashi-Lufubu Area. Note the hills of granite in the Basement Schists in vicinity of 16 Shaft and Irwin Shaft were originally considered to be intrusions of "Younger" Granite removing portions of the Lower Roan sediments by magmatic stoping.

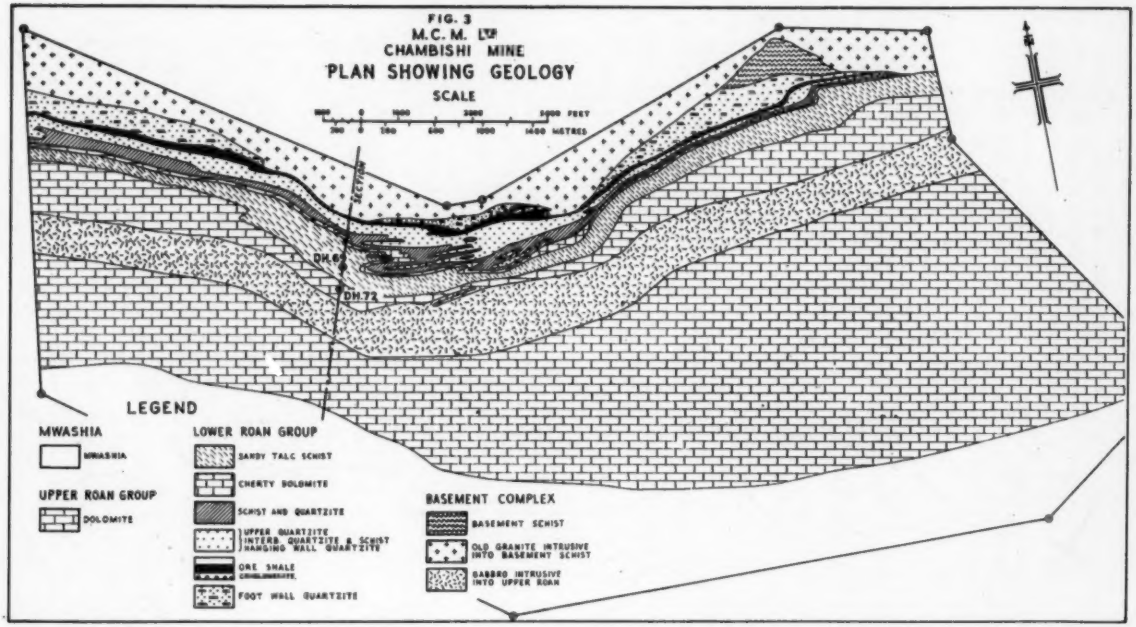

FIG. 3. Geological map of Chambishi. This is essentially the careful mapping of Dr. D. M. Davidson under the supervision of Dr. Anton Gray.

younger red granite is not known, as these two intrusives have not been observed in contact with one another." He describes the different types of granite in great detail and attributes the copper mineralization to be due to both the "younger" varieties.

SUMMARY OF EVIDENCE FOR A YOUNGER GRANITE.

From the above descriptions it would appear that the following criteria have been used by the past authors in determining the presence of this Younger Granite:

(1). Presence of narrow pegmatite dikes, veins, etc., containing copper sulfides in the Roan Series and granites.
(2). Granite believed to have cut out, in the case of the Roan Antelope, several hundred feet of footwall sediments and a portion of the copper-bearing horizon, and at Chambishi all the footwall rocks in several places.
(3). The granite carries traces of copper.
(4). Relation of the ore shoot to the granite at Chambishi and Mufulira.
(5). Metamorphism of Roan Series in the vicinity of the granite.

EVIDENCE AGAINST A YOUNGER GRANITE.

The writers will now discuss the evidence against these so-called Younger Granites from three localities where, from the above literature, they have been assumed to be present. The writers further maintain that there is no real evidence for a Younger Granite in the Copperbelt. All the so-called Younger grey and pink granites are simply variations of the Older Granite, of which there are many different types and ages.

The locations selected to refute the evidence for a Younger Granite are the Roan Antelope, Chambishi, and Mufulira Copper Mines, which will now be discussed in that order.

Roan Antelope.

The presence of a younger granite was first suspected when surface diamond drilling in the 16 Shaft area passed from the ore horizon into a pink granite without intersecting the normal footwall beds. This granite differed from the normal grey granite in color and texture. In addition, in this area, the ore "shales" were very highly metamorphosed between the two granite masses situated to the north and south of the syncline. This metamorphism was attributed to the heating effects of the intrusive granite, i.e., contact metamorphism. Furthermore, the drill holes intersected numerous small quartz-feldspar veins, resembling pegmatites, containing irregular masses of copper sulfides. All the data seemed to indicate an intrusive granite and are summarized below:

(a) a pink granite instead of the normal grey granite.
(b) absence of the usual footwall sediments presumed to have been removed by magmatic stoping.
(c) high degree of metamorphism of the Roan sediments, especially the ore horizon in the vicinity of the granite.
(d) presence of veins resembling pegmatites.

These observations all strongly support the case for a younger intrusive. Underground development, however, has brought to light new data that has changed the picture completely.

Color of the Granite.—It appears that the pink granite is simply a marginal variety of the grey granite that occurs in the 16 Shaft area. The two types can be seen underground to grade into each other. The pink type may represent a later alteration phase of the Old Grey Granite.

Absence of the Footwall Quartzite Horizon.—The absence of this horizon is due to the uneven land surface present during the time of the deposition of the Roan sediments. In this case it was cut out by the granite hill that was overlapped by the ore horizon. This is clearly illustrated by Figures 4 and 5. Hollows in this granite land surface contain small local basins of footwall quartzites and conglomerates.

Granite boulders are very conspicuous in the conglomerate bands of the footwall quartzites. These conglomerates attain a remarkable development in local hollows between the granite hills.

Degree of Metamorphism.—The normal ore-bearing argillite has been metamorphosed to a biotite schist, a banded biotite-calc schist, etc. These alterations are due to the greater intensity of regional metamorphism produced

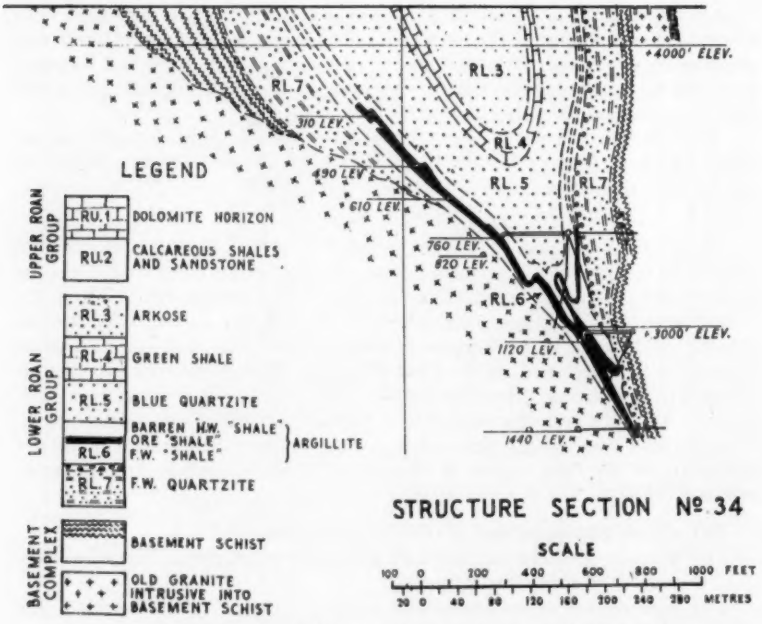

FIG. 4. Structure Section 34 showing how thickness of the R.L.7 horizon is cut out by Old Granite hill.

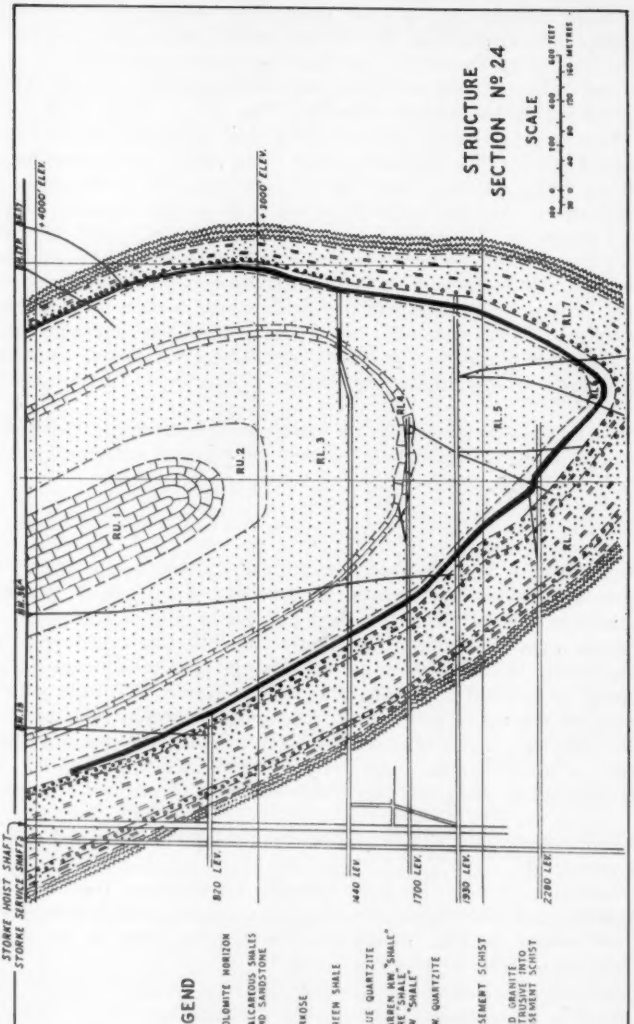

FIG. 5. Structure Section 24. This represents a normal section of the sediments where unaffected by the presence of granite hills.

by compression between the two granite buttresses situated on either side of the syncline. The intensity of the metamorphism and drag-folding can be seen to decrease along the strike away from the granite buttresses.

Veins and Dikes.—These veins have been called pseudo-pegmatites as they resemble true pegmatites in many respects. They are the by-product of folding and reach their best development in the highly folded area in the vicinity of 16 Shaft (Fig. 4). The veins are similar to the Alpine mineralized fissures described by Niggli, Parker and others.[9] Underground development has shown conclusively that the grade of the ore is in no way dependent on the presence of the veins. These veins are not derived from the granite but obtain their filling by a process of lateral secretion from their immediate wall rock.

Aplites.—Rocks resembling aplites in composition and appearance have been found in some of the sediments. On first examination they appear to resemble aplites. They commonly contain fragments of the underlying shales. Closer examination proves them to be re-crystallized gritty arkoses containing desiccation flakes of the underlying shales. They show "scour and fill" features.

Conclusions.—All the criteria for the existence of the Younger Granite have been shown to be due to depositional features and regional metamorphism and no Younger Granite is observable in the Roan Antelope district.

Chambishi.

The senior author has been associated with this problem since 1929. The following evidence is believed to be a fair summary of the salient features of the evidence available in 1930 for considering the granite at Chambishi and the contiguous Special Grants to be intrusive into the Roan sediments: (1) "intrusion breccia" at Chambishi Mine; (2) uneven granite-sediment contact; (3) "stoping" of footwall sediments, bringing the granite in contact with the ore shales; (4) relation of ore shoot to proximity of granite, similar to the relation at Mufulira; (5) peculiar sediment-granite contact found in prospecting pit west of Chambishi and interpreted as being intrusive (Fig. 6); (6) pegmatites and quartz veins carrying copper sulfides and ascribed to intrusive granite.

The above evidence will now be reviewed in the light of the new data accumulating since 1931.

The "Intrusion Breccia" has been observed elsewhere on the Copperbelt and fresh underground exposures show that it is a conglomerate or breccia with recrystallized arkosic matrix. Some cross bedding in lenses of this matrix demonstrates its original sedimentary origin.

Uneven Granite-Sediment Contact and "Stoping" of the Footwall Sediments.—At all of the mines in the Copperbelt the early Roan land surface has been demonstrated to represent a very rough topography showing many steep sided hills of the harder basement rocks, as beautifully exemplified at Mufulira by the hills of "Muva Quartzite" projecting up to the ore horizon. On the

[9] Niggli, P., Koenigsberger, J., and Parker, R. L., Die Mineralien der Schweizeralpen, Basel, B. Wepf & Co., Band I and II, 1940.

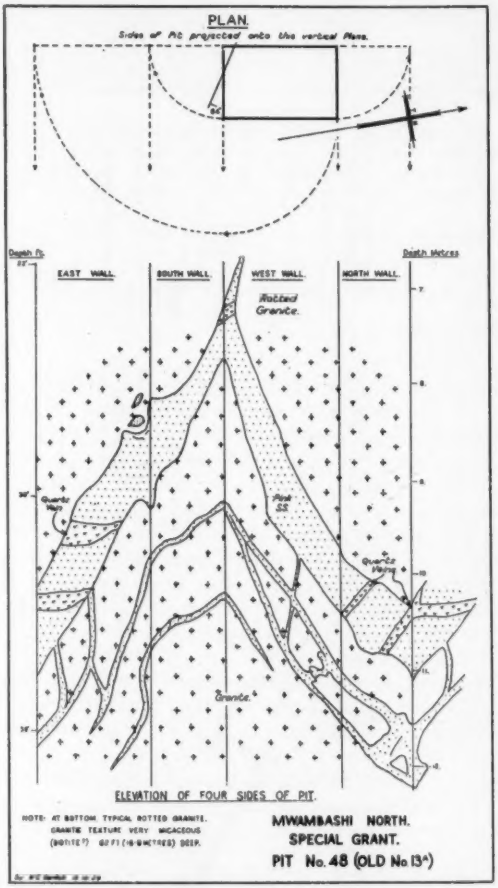

FIG. 6. Details of the geology exposed in a pit on the Mwambashi North Special Grant. The granite was originally logged as intrusive into the pink sandstone (Lower Roan), which is now interpreted as being a sand filling between exfoliating slabs of granite on an old land surface. The quartz veins are due to lateral secretion filling of cracks formed in the sandstone during diagenesis and regional metamorphism. They are confined to the more brittle sandstone.

flanks of these ridges, basal breccias and conglomerates formed, and the hollows between were filled with basal conglomerate and aeolian deposits.

That the granite at Chambishi also formed hills on this old land surface is shown by the following data (fig. 7):

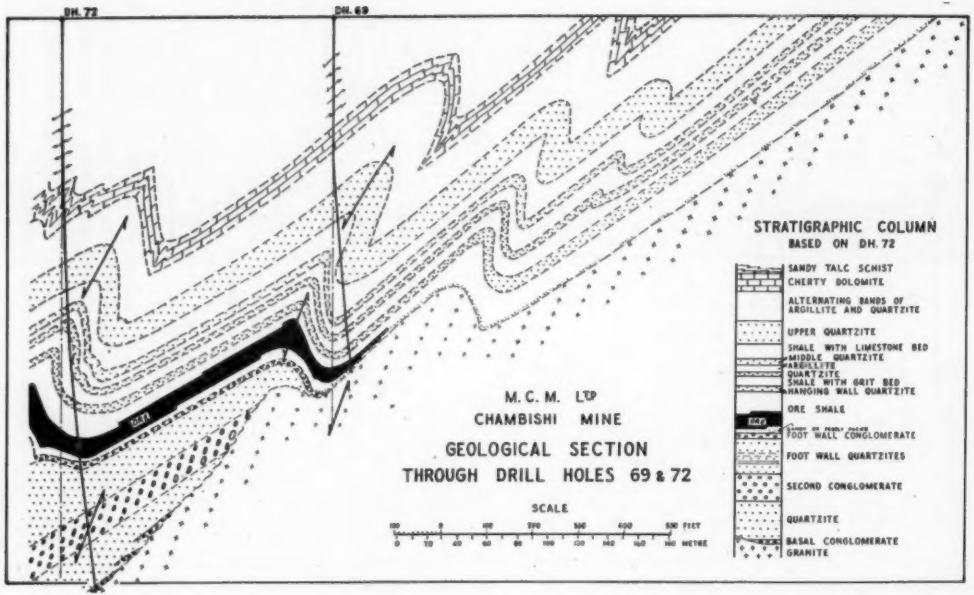

FIG. 7. Geological section through Drill Holes 69 and 72. The parallelism of the foliation of the granite, the cleavage of the shales, and the axial planes of the drag folds is indicated. The thinning of the ore shale with development of sandy and pebbly facies at the contact with the bevelled top of the granite hill is shown. The termination of the ore against the shallow water facies is indicated.

Where the footwall sediments of the ore shales are developed a conglomerate rests immediately on the granite.

Where the ore horizon is in direct contact with the granite there is a lateral change in facies from deep water sediment to shallow water sediment. Generally a residual arkose or a thin conglomerate intervenes between the sandy shales and the granite.

Where the footwall sediments are absent, the ore shales are more strongly metamorphosed, but the change is purely dynamic, resulting in a well cleaved argillite, phyllite, or biotite schist. However, the biotite schist zone is best developed in the deeper water sediments near the base of the ore shales, distant from the granite hill.

No contact metamorphic minerals such as andalusite or cordierite have ever been recorded at Chambishi.

Pegmatites and aplites are relatively rare in the Chambishi granite. The fairly numerous granulated quartz veins terminate at the contact with the overlying sediments.

The granite of the boulders in the conglomerates is indistinguishable from the underlying granite.

Relation of Ore Shoot to Granite.—The ore shoot at Mufulira occupies a shallow basin developed on Basement schist between two bodies of granite. The main ore body at Chambishi overlies footwall quartzites and conglomerates occupying a basin over granite between two protrusions of granite projecting up to the ore horizon. The ore cuts out in the vicinity of these "protrusions" of granite, not because of any heat effects of a Younger intrusive, but because of change of facies of the ore shales, *viz.*, the ore shales become more coarsely sandy or even pebbly against these "promontories" of granite projecting southwestward into the sea or lake in which the ore shales were deposited. Recent drilling has indicated that these promontories have limited extension down dip.

Sediment-Granite Contact Exposed in Pit.—The peculiar sediment-granite contact exposed in a prospecting pit (Fig. 6) was interpreted in 1930 as being due to injection of lenses of granitic magma between the bedding planes of the Lower Roan feldspathic quartzite. It is now interpreted much more simply and without violating so many laws of mechanics, as being due to infiltration of sand under exfoliated slabs of hard granite on the early Roan land surface. This phenomenon has been beautifully exposed by underground development on certain of the other Copperbelt mines.

There are conspicuous cracks, now filled with quartzites, by which the sand gained access to the cavities below the exfoliation blisters. Similar sand filled cracks are shown in the sketch made by the writer in 1929.

Pegmatites and Veins.—The pegmatites and quartz veins have been briefly described for the Roan Antelope, so the intention is here to stress only the general features which indicate their origin by regional metamorphism instead of magmatic injection.

The following features are observable at all the Copperbelt mines with only minor variations from mine to mine:

(a) The *Paragenesis* and mineral content remove these "pseudo-pegmatites" from the class of pegmatites of magmatic origin. Omitting the rarer minerals, the paragenesis is from earliest to latest crystallization, specularite, anhydrite, feldspar, dolomite, quartz, pyrite, chalcopyrite, bornite, chalcocite, chlorite, calcite. The rarer minerals, not in order of paragenesis, include:

tourmaline, rutile, carrollite, muscovite, pyrrhotite. The feldspar includes albite and potash feldspar generally of the adularia habit.

(b) *The Occurrence and Relative Abundance of the Minerals* depend very conspicuously on the host rock and the following is only a generalization:

	Host Rocks	Vein Minerals in Order of Abundance
	Mwashia shales (pyritic)	*Dolomite*, pyrite, pyrrhotite
Upper Roan	Shales and schists	*Dolomite*, quartz
	Dolomite (often cherty)	*Quartz, dolomite*, pyrite
Lower Roan	Arkoses	*Quartz, specularite*, anhydrite
	Evaporites (porous sand stones)	*Anhydrite, dolomite*, feldspar, quartz
	"Barren shales"	*Quartz, feldspar, specularite*, dolomite
	"Ore shales"	*Quartz, feldspar, dolomite, anhydrite, bornite* and *chalcopyrite*
	Quartzite	*Quartz*, anhydrite, feldspar, specularite
	Basement (to 300 feet below unconformity)	Quartz, anhydrite, dolomite, specularite

As noted above, these pseudo-pegmatites and veins associated with the folding of the Katanga System can be traced down for a short distance into the Basement Complex where they contrast with and cut the older granulated quartz veins and the generally recrystallized old pegmatites with coarse tourmaline and books of muscovite.

(c) *The Distribution and Habit of the Veins*, through ten years of study, prove that they are similar to the Alpine mineralized fissures and were produced by fracturing and "lateral secretion" in the Katanga System and adjacent Basement due to the strong horizontal forces. These forces caused the thrust faults in the Katanga area, the deep infolds in Northern Rhodesia and the general arcuate arrangement of this ancient mountain system in the Congo and Northern Rhodesia.

The veins are generally lenticular, short and unconnected, often with a 1 to 5 cm zone of leaching in the wall rock. They can be classified as below:

(1). *"Gash" veins in brittle rocks:* generally short "gash" veins perpendicular to fold axes in quartzites, arkoses, etc.
(2). *Saddle reefs* along bedding contacts opened by fold movements.
(3). *Lenticular veins along shear zones* generally showing en echelon arrangement.
(4). *Bedding veinlets* occupying especially the opened laminations in shales.
(5). *Continuous quartz veins* in opened shear joints.

The "gash" veins are mostly only a few cm thick but may reach 50 cm thick and 30 cm in length. They generally terminate abruptly on entering a less competent formation.

The saddle reefs and veins in the shear zones may have considerable linear dimensions.

All the above, with the bedding veinlets, contain copper sulfides only where they are enclosed by, or contact, the ore horizon.

The continuous quartz veins may have very great extension in two dimensions, but they are mostly less than 20 cm thick and contain only a little dolomite or calcite, besides quartz. They are commonly later in age than the other veins.

(d) *The Origin* of these pseudo-pegmatites and veins, as previously stated, is due to the metamorphism resulting from the folding of the sediments. They derive their mineral content by migration of connate solutions from the adjacent wall rock into the various types of fissures produced during folding.

Conclusions.—The various criteria for the Younger Granite have thus been refuted. The "Intrusion Breccia" was a case of mistaken identification of a deeply weathered rock. The stoping of the footwall sediments was a misinterpretation of the uneven granite-sediment contact. The relation of the ore shoot to the granite can be explained by at least three different theories. The granite contact exposed in a pit was misinterpreted originally by the senior author. The pegmatites and veins in the Katanga sediments in the Copperbelt are not of magmatic derivation.

Mufulira.

The chief facts quoted in favor of the Younger Granite are as follows: (1). Genetic relation to the mineralization of the "younger grey granite"; (2). Occurrence of copper-bearing veins and stockworks in the schists near the granite margins; (3). Occurrence of silicified quartzite, with numerous quartz veins and granite dikes and a block of this presumed Lower Roan quartzites in the Mufulira West granite; (4). Metamorphism of the Katanga sediments attributed to the intrusion of the granite.

Underground development, plus additional surface prospecting, has yielded the following evidence on the subject:

Unconformity at Mufulira East.—Recent pitting on the eastern portion of the Mufulira grant has exposed a sedimentary contact between the Katanga sediments and the granite. Here, the Roan footwall sediments, resting in a hollow on the granite, show a lenticular granite boulder bed.

Unconformity at Mufulira West.—Detailed mapping in the Mufulira stream area has also demonstrated a similar unconformity. Here a considerable fold, with local overturning of the beds, was originally attributed to the intrusive action of the granite, but is now explained as being emphasized by the buttress effect of the granite hill. A similar fold occurs in the mine opposite the hill of the Basement "quartzite."

Boulders of Granite in Basal Conglomerate.—The granite has been exposed underground on the 1,400′ level. Here it intrudes only the Basement "quartzites" and boulders of this granite have been found in the Roan basal conglomerate.

Age of the Mineralization.—Underground exposures have shown the mineralization of the sediments to be pre-folding with a certain amount of migration of the sulfides into fractures, or joints, produced by folding.

Veins.—No veins have yet been observed underground to pass from the Basement into the Roan sediments along which mineralizing fluids could have flowed. Small veins, however, are found in the rocks of both systems. The veins in the Katanga sediments are of the same mode of origin as those found

at the Roan Antelope and Chambishi. As these sediments are not as highly drag folded as are those at Roan Extension, the veins are not nearly as common nor of such large dimensions.

The veins in the Basement chloritic quartzites are true pegmatites that originated from the intrusion of the Old Granite. Copper occurs in the pegmatites and also along small fissures. The copper has been derived from the Granite.

Those in the Roan sediments have derived their copper from the disseminated sulfides present in the surrounding sediments, as proved by the restriction of copper sulfides to those veins intersecting the mineralized horizons.

Metamorphism.—The metamorphism of the Roan sediments has been demonstrated to be due to the regional metamorphism produced by the folding of the sediments.

Quartzite Inclusions in the Granite.—The granite contains many xenoliths, none of which can be identified with the Katanga System. The Roan sediments adjacent to the granites are no more silicified than elsewhere. The numerous veins are due to fracturing on the sharp fold in this vicinity. No granite dikes have ever been observed by us in the Katanga System and hence the reference of Anton Gray's is believed to refer to the Basement.

Conclusions.—The above features all indicate that the only granite observed to date is of pre-Katanga age, that the mineralization is pre-folding and that the veins and degree of metamorphism are attributable to the folding.

OTHER MINES AND PROSPECTS IN THE COPPPERBELT.

Recent work on the other Special Grants on the Copperbelt held by Mufulira Copper Mines, Limited, has to date not disclosed any evidence to suggest the presence of a Younger Granite. The senior author, who was a geologist at Nkana during the period 1940 to 1946, states that no Younger Granite has been found on that property. Dr. J. J. Marais, former geologist to Nchanga, also maintains that no Younger Granite is present on that property to the best of his knowledge.

AGE OF THE GRANITES.

The paper so far has been concentrated on clarifying one major point, *viz.*, that there is no Younger Granite on the Copperbelt. Some writers, Jackson in particular, distinguish several types of Older Granite. No mention, however, is made of the absolute age of these granites.

The Katanga System overlies the Basement Complex. This is a general term which has been applied to all rock types older than the Katanga System. Anton Gray [10] distinguishes between two systems both older than the Katanga, *viz.*, the Muva System and the Lufubu System. These two Basement Systems are composed chiefly of mica and chlorite schists with few outcrops. The Muva System, however, has a very important marker horizon in a band of white resistant quartzites known as the Muva Quartzites. The schistose mem-

[10] Gray, Anton, The correlation of the ore-bearing sediments of the Katanga and Rhodesian Copperbelt: ECON. GEOL., vol. 25, p. 788, 1930.

bers are difficult to distinguish in the field in the absence of the Muva Quartzite horizon. The Lufubu schists contain abundant pegmatites and are generally highly contorted. No granite has yet been observed to be intruded into the Muva Quartzites on the Copperbelt.

With the data now available the writers believe that only the Lufubu System has been intruded by the Old Granite and hence date the Old Granite to be post-Lufubu System and pre-Muva System. However, the Nchanga red granite and the Muliashi porphyroblastic gneiss have not been seen in contact with the Muva System and may possibly intrude it.

In view of the above data, the authors wish to offer the following revised stratigraphic column:

Revised Stratigraphic Column as at 1950.

System	Series	Group	Formations
Katanga	Kundelungu		Quartzites, shales, dolomite and tillites
	Mine	Mwashia	Sandstones and shales
		Upper Roan	Dolomites and shales
		Lower Roan	Dolomites, shales, quartzites, arkoses and conglomerates
		Unconformity.	
Muva			Schists and quartzites
		Unconformity.	
Lufubu			Schists and gneisses

Old Granite intrusive into Lufubu System.
Gabbro intrusive into Upper Roan Group.

APPENDIX—DESCRIPTION OF CHAMBISHI GRANITE.

Introduction.—This description of the megascopic features of the Chambishi granite is not essential to this paper on the age of the granites. It may, however, be of value in recognition of the Old Granite elsewhere and the evidence here recorded furthers the argument in favor of the absence of a Younger Granite. It was due to similar observations on other granites in the Copperbelt that caused the re-opening of the problem in 1940.

Structural Environment.—At Chambishi West the ore shales have a well developed cleavage dipping in a direction a little west of south, parallel to the axial planes of the drag folds. The axes of these drag folds have a very constant plunge of close to 20° in a direction nearly due west.

The formations below the ore shales, whether granite, arenaceous sediment or conglomerate, show parallel structures to these in the ore shales and these structures have been of economic value in interpreting the folded nature of the Chambishi ore body.

The cleavage of the shales and the foliation of the dolomitic sandstones and conglomerates and of the Chambishi granite are to be ascribed to dynamic metamorphism, with the appropriate recrystallization and metamorphism cor-

responding to the depth of burial of the sediments at that time. The argillaceous sediments are in the "Biotite Zone" of the dynamothermal metamorphic sequence.

The response of the granite to these same forces is interesting and may be utilized in the recognition of the "Old Granite."

Texture of the Highly Sheared Granite.—Near the unconformity the effects of the shearing stresses are most obvious. Here the original feldspars have been entirely converted to sericite, the quartz has been granulated, and the biotite has been finely crushed or granulated and squeezed into irregular nests and wisps between the other minerals. The original feldspars are thus represented by flattened areas of sericitic schist, with a silky phyllitic or even oily appearance. The original quartz grains are represented by ovoid areas of finely granular quartz, but the centers of these ovoids are commonly more coarsely granular opalescent quartz, possibly due to subsequent recrystallization. The original biotite crystals are thoroughly mashed and show no attempt at recrystallization, and only a crude orientation by elongation of the nests or wisps of structureless biotite.

The rock has only a ghost-like texture of the original granite and the term orthogneiss is useful in describing the rock. The gneissose structure is not too strongly developed, but along shear zones a phyllitic appearance is noticed. Old quartz veins have been completely and finely granulated. In some of the shear zones a regrowth of the feldspar from the sericite has taken place, giving small feldspar porphyroblasts.

The gneissose structure of this orthogneiss dips steeply south and the minute corrugations of the phyllitic patches plunge to the west.

Texture of Normal Granite.—About 100 to 200 feet below the unconformity the effects of shearing are much less evident. The feldspars have regrown in the centers of the sericitic areas and have a milky to greasy luster, somewhat difficult to distinguish from the quartz. The quartz areas are still granular but the opalescent centers are still more conspicuous. The nests of biotite have still a "dead" appearance, but occasionally the growth of the feldspars has included minute flakes of biotite and pushed the rest of the material aside. The rock now has the appearance of a normal grey granite and only the nests of crushed biotite and the preferred breakage along sericitic films anastomosing between the granules of the rock indicate that this granite may have suffered the same dynamothermal metamorphism as the "orthogneiss" above. The development of occasional feldspar porphyroblasts, commonly tinged pink by scales of hematite, demonstrates further the recrystallization under more static metamorphic conditions after the dynamic stage.

The chemistry of the process is believed to be as follows:

$$\text{Feldspar} + \text{water} \xrightarrow{\text{stress}} \text{Sericite or Paragonite} + \text{alkali} + \text{silica}.$$

$$6(K_2O\cdot Al_2O_3\cdot 6SiO_2) + 4H_2O \longrightarrow 2(2H_2O\cdot K_2O\cdot 3Al_2O_3\cdot 6SiO_2) + 4K_2O + 24SiO_2.$$

$$6(Na_2O\cdot Al_2O_3\cdot 6SiO_2) + 4H_2O \longrightarrow 2(2H_2O\cdot Na_2O\cdot 3Al_2O_3\cdot 6SiO_2) + 4Na_2O + 24SiO_2.$$

Thus the process needs two molecules of water for each feldspar molecule and such quantities of water are not available in a normal granite, unless it has been considerably weathered or contains ground water along opened joints and shears. The latter would also be necessary for the release of alkali and silica. Hence the "orthogneiss" stage is restricted to shear zones and to the originally weathered zone at the unconformity with the Katanga System.

In the normal granite distant from the old land surface the development of sericite is inhibited. When it is formed under intense shear it readily reverts back to feldspar unless the alkali and silica can escape:

$$\text{Sericite} + \text{alkali} + \text{silica} \longrightarrow \text{feldspar} + \text{water}.$$

This mechanism may promote the formation of porphyroblastic feldspars, as the little available water is passed on from the crystallizing porphyroblast to the adjacent stressed feldspar. Some sericite survives as flakes in the feldspar and as films between the grains and along zones of more intense shear.

These or similar processes have been observed in the other granites of the Kafue anticline and wherever the "Old Granites" in Northern Rhodesia are adjacent to the strongly folded Katanga System. The same phenomena should be observable in the Mokambo and Luina[11] domes in the adjacent Belgian Congo.

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MUFULIRA, NORTHERN RHODESIA,
Jan. 10, 1951.

[11] Headwaters of Luina River.

PHYSICAL CHEMISTRY OF QUICKSILVER TRANSPORTATION IN VEIN FLUIDS.

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ABSTRACT.

Possible mechanisms for the transportation of quicksilver in vein fluids are examined by the methods of chemical thermodynamics. Mechanisms shown to be impossible are those depending on decrease of ionization or solubility of H_2S at high temperatures, on elimination of H_2S at high temperatures by displacement of equilibrium in the gas phase, and on the formation of complex mercury-halogen complex ions. Mechanisms shown to be feasible are transportation as HgS_2^{--} in alkaline sulfide solutions, as the volatile chloride in the vapor phase, and as the vapor of the element itself. Data are conflicting about the possibility of transportation in acid or neutral solutions as a sulfomercuric acid. Transportation as the sulfide in supersaturated solutions or as a colloidal dispersion seems possible, but cannot be quantitatively evaluated from present data.

A reasonable explanation for the separation of cinnabar deposits from deposits of most other sulfide ores is the thermal instability of mercuric sulfide. At temperatures over 250° C the sulfide cannot exist in the presence of a moving vapor, unless concentrations of mercury and sulfur vapors are improbably high. Even at temperatures well below this point mercury and sulfur can be carried in appreciable concentrations in a moving vapor.

INTRODUCTION.

QUICKSILVER ores, it is generally agreed, are formed by deposition from vein fluids at temperatures not as low as 80° nor as high as 250° C, and at pressures below 30 atmospheres. The geologic evidence for these conclusions has been summarized by Dreyer (1)[1] and Thompson (2). With the conditions of formation so sharply delimited, it should seemingly be possible to specify with some exactness the nature of the vein-forming fluids. The fluid most commonly postulated is one containing an excess of sulfide ion, necessarily alkaline because sulfide ion is stable only in the presence of hydroxide ion, such a solution holding mercury in the form of a complex ion, probably HgS_2^{--}. This hypothesis was first elaborated by Becker (3) and has been ably supported by Dreyer. Recently dissatisfaction has been expressed with the alkaline sulfide concept, on the grounds that accessible natural solutions which should most closely resemble vein solutions (hot spring waters and fluid inclusions in vein minerals) have compositions quite different from the postulated alkaline sulfide waters (Yates and Thompson (4), White (5)).

Enough chemical data on the behavior of mercuric sulfide have been accumulated so that it should be possible to test the adequacy of the alkaline sulfide hypothesis and of various other possible mechanisms of transporta-

[1] Figures in parentheses refer to Bibliography at end of paper.

tion. Some of this testing has been done by Dreyer (1); his paper should be referred to for a critique of the alkaline sulfide postulate on geologic and qualitative chemical grounds. Dreyer's paper, together with papers by Thompson (2) and Ross (6), will serve also to summarize available geologic data on quicksilver deposits; these data will not be repeated here. The purpose of this paper is to explore strictly chemical data on mercury with the idea of delimiting quantitatively, insofar as possible, the physical-chemical conditions of quicksilver deposition. It may be said at the outset that chemical data at present do not suffice to solve the problem completely, but at least help to make some mechanisms far more probable than others.

CHEMICAL DATA AND ASSUMPTIONS.

Some of the chemical data which will be used in evaluating the possible mechanisms require a brief preliminary discussion. Data which are used for only a single mechanism are discussed in the section to which they directly apply.

Solubility Product of Mercuric Sulfide.—The value most commonly used in the literature is 2.8×10^{-54} at 25° C, originally determined by Knox (7) from measurements of solubility in alkaline sulfide solutions and accepted as the best value in a critical discussion by Kolthoff (8). More recently Treadwell and Schaufelberger (9) have obtained a higher value, 7×10^{-53} for cinnabar and 3×10^{-52} for metacinnabar (at 18° C), from measurements of the equilibrium between HgS and H_2. Measurements of the vapor pressure of HgS by Rinse (10) make possible another computation of this constant, about 10^{-55}. Verhoogen (11) uses a much higher value, 10^{-47}, but does not quote his source. In this paper the figure given by Treadwell and Schaufelberger for cinnabar, 7×10^{-53}, will be used.

Solubility of Mercuric Sulfide.—The solubility of HgS is not the simple square root of the solubility product, but is increased by the hydrolysis of sulfide ion. Both Kolthoff and Verhoogen have deduced formulas giving the necessary correction. Verhoogen's calculations give 1×10^{-17} grams/liter at 25° and Kolthoff's give $10^{-22.67}$ moles/liter at 18°, for the solubility in pure water. If the above value of the solubility product is substituted for the ones used by Verhoogen and Kolthoff, both methods of calculation give a solubility of about 10^{-22} moles/liter at ordinary temperatures. The hydrolysis of sulfide ion is increased if the water contains CO_2, because of the greater amount of hydrogen ion available. For water in equilibrium with atmospheric CO_2, the solubility is about 10 times as great as for pure water; for water in equilibrium with CO_2 at 1 atmosphere pressure, the solubility is about 1,000 times as great.

Ionization Constants of Hydrosulfuric Acid.—Hydrogen sulfide in solution forms a weak acid, ionizing according to the steps

$$H_2S = H^+ + HS^-;\ K_{H_2S} = \frac{(H^+)\ (HS^-)}{(H_2S)},$$

$$HS^- = H^+ + S^{--};\ K_{HS^-} = \frac{(H^+)\ (S^{--})}{(HS^-)}.$$

(Parentheses around formulas of molecules and ions refer to activities or concentrations.) The most recent determinations of these constants, made by Kubli (12) by measurements of pH with a glass electrode, give 0.87×10^{-7} for the first and 0.36×10^{-12} for the second. Earlier work is discussed in detail by Kubli; published values of the first constant have ranged from 0.57×10^{-7} to 3.3×10^{-7} and of the second from 1.2×10^{-15} to 6×10^{-14}. For present purposes approximate values close to these given by Kubli will be used: 10^{-7} for the first constant and 10^{-13} for the second.

It should be emphasized that numerical accuracy is not an object in the following discussion of mechanisms of transport. As illustrated above, the basic chemical data are not in close agreement, and some of the geologic factors are even more uncertain. The best that can be hoped for is a series of approximate numbers expressing the order of magnitude of the solubilities, stabilities, and volatilities of mercury compounds under various conditions. Such order-of-magnitude figures will be sufficient to eliminate some mechanisms from consideration and to demonstrate the feasibility of others, but no importance should be attached to the specific numbers derived.

POSSIBLE MECHANISMS.

The problem is to delimit as far as possible the composition and physical state of a fluid capable of transporting mercury at temperatures higher than 250° C and pressures greater than 30 atmospheres, and of depositing the mercury as the sulfide when the temperature falls, when the pressure or acidity changes, or when the fluid is diluted. The possible mechanisms will be considered in this order:

(1) HgS may be simply carried in solution, no ions except the ions of water appreciably affecting its solubility.

(2) Mercury may be carried in solution in the form of a complex sulfide ion, from which the simple sulfide is precipitated whenever the concentration of free sulfide ion is reduced.

(3) Mercury may be carried in solution as a sulfo-mercuric acid, such as H_2HgS_2, from which the sulfide would be precipitated when H_2S escapes from solution.

(4) Mercury may be carried in solution in the form of a complex chloride ion, from which the sulfide may be precipitated on dilution.

(5) Mercury may be carried in solution in the presence of H_2S, the precipitation of HgS being prevented at high temperatures by a low degree of ionization of H_2S.

(6) Mercury may be carried in a solution accompanied by H_2S in the gas phase, the solubility of H_2S being too small at high temperatures to precipitate HgS.

(7) Mercury may be carried in a solution accompanied by a gas phase, the amount of H_2S in the gas being kept low at temperatures above 200° by reversible reactions with other gases.

(8) Mercury may be carried in the vapor phase as $HgCl_2$, the sulfide precipitating when the vapor condenses or cools.

(9) Mercury may be carried in the vapor phase as free Hg, accompanied

by sulfur vapor, and may be deposited as HgS directly out of the vapor or out of a solution accompanying the vapor.

FIRST MECHANISM: THE SOLUBILITY OF HgS.

If the solubility of HgS in water at equilibrium with atmospheric CO_2 is 10^{-21} moles/liter at ordinary temperatures (see above), Verhoogen's (11) calculations indicate that the solubility would be on the order of 100 times as great at 400° C. At this temperature, then, a saturated solution would contain roughly 10^{-19} moles, or 10^{-17} grams per liter. Practically all of this could be deposited as the solution cools. In order to deposit one gram, at least 10^{17} liters would have to pass through a fissure; to deposit one ton, at least 10^{23} liters. A volume of 10^{23} liters is approximately 100 times the volume of water in all the oceans.

Such figures are patently absurd, but it is difficult to specify just how much higher the concentration should be in order to be considered reasonable. A solution containing, say, 10^{-7} grams per liter of mercury would be capable of depositing 1 gram from every 10^{7} liters or 1 ton from every 10^{13} liters, roughly the amount of water flowing in the lower Hudson River per year (average flow on the order of 10,000 second-feet). A solution of this concentration flowing through a vein at a rate of 10 second-feet could deposit one ton of mercury in a thousand years. This rate of flow seems excessive, so perhaps 10^{-7} grams/liter may be taken as a safe minimum concentration. The solubility of HgS in pure water or in water containing CO_2 falls far short of this figure.

SECOND MECHANISM: ALKALINE SULFIDE SOLUTIONS.

Sulfide solutions of moderate to high pH are the classical answer to the problem of mercury transportation. The best quantitative work on the solubility of HgS in such solutions is apparently still that of Knox (7), done in 1906. Some of Knox's measurements have been repeated recently by Saukov (13), who reports solubilities a little smaller than those given by Knox. Dreyer (1) has used Knox's figures as a basis for a detailed qualitative discussion of the alkaline sulfide mechanism, and Garrels (14) has outlined a method for calculating from chemical data the solubility of any metal sulfide in excess sulfide ion at various values of pH. The calculations which follow are essentially an application of Garrels' method to the data of Knox and Saukov.

Let us assume that mercury dissolves as the ion HgS_2^{--}. More complex ions are possible, but in the absence of definite information the simplest ion will serve as well as any other; the choice of ion does not greatly affect the resulting solubility figures. The principal equilibria in a sulfide solution in contact with HgS may then be written:

$$HgS = Hg^{++} + S^{--}, \quad (1)$$

$$HgS_2^{--} = Hg^{++} + 2S^{--}, \quad (2)$$

$$HS^{-} = H^{+} + S^{--}, \quad (3)$$

$$H_2S = H^{+} + HS^{-}. \quad (4)$$

The corresponding equilibrium constants are

$$(Hg^{++})\,(S^{--}) = K_1,$$

$$\frac{(Hg^{++})\,(S^{--})^2}{(HgS_2^{--})} = K_2,$$

$$\frac{(H^+)\,(S^{--})}{(HS^-)} = K_3,$$

$$\frac{(H^+)\,(HS^-)}{H_2S} = K_4.$$

One further equation must be satisfied:

$$(HS^-) + (H_2S) + (2HgS_2^{--}) + (S^{--}) = S_{total},$$

which merely expresses the fact that the dissolved sulfur is present as four different substances (excluding sulfate, thiosulfate, etc.). Equations (1) to (4) may be combined to give

$$S_{total} = (S^{--})\left(\frac{(H^+)}{K_3} + \frac{(H^+)^2}{K_3K_4} + 2\frac{K_1}{K_2} + 1\right). \tag{5}$$

If now we can assign values to K_3, K_4, and the ratio K_1/K_2, this equation permits us to calculate (S^{--}) for any given solution of known pH and known total sulfur. From (S^{--}) we can obtain (HgS_2^{--}) by the relation

$$(HgS_2^{--}) = \frac{K_1}{K_2}(S^{--}). \tag{6}$$

This is practically equal to total dissolved HgS, since the amount of free Hg^{++} is negligibly small even at low pH's.

Knox determined K_3 and K_1/K_2 ingeniously by measuring (Hg^{++}) electrometrically and then choosing the value of K_3 which gave the most nearly constant values of K_1 and K_2. In order to use Saukov's solubility figures and Kubli's (12) determinations of K_3 and K_4, we shall use a different procedure: K_3 and K_4 will be considered as known (10^{-13} and 10^{-7}, respectively), and K_1/K_2 will be found by substituting experimentally determined values of S_{total}, (H^+) and (HgS_2^{--}) in equations (5) and (6). It turns out that the solubilities of HgS calculated in this way are actually not very different from those using Knox's estimates for the constants.

Let us take 0.007 mole/liter as an average value for the solubility of HgS in 0.1 *M* Na_2S (Knox: 0.008241; Saukov: 0.0060). Hydrolysis of S^{--} gives the solution a pH of approximately 13. Equation (5) is therefore

$$0.1 + 0.007 = (S^{--})\left(\frac{10^{-13}}{10^{-13}} + \frac{(10^{-13})^2}{10^{-13}\cdot 10^{-7}} + 2\frac{K_1}{K_2} + 1\right).$$

For S^{--} this gives

$$(S^{--}) = \frac{0.107}{2\dfrac{K_1}{K_2} + 2}.$$

Then from equation (6):

$$HgS_2^{--} = 0.007 = \frac{K_1}{K_2}\left(\frac{0.107}{2\frac{K_1}{K_2} + 2}\right)$$

from which

$$K_1/K_2 = 0.15.$$

By using this figure in equations (5) and (6) for other values of pH and total S, we obtain the solubilities in columns 2 and 4 of Table I. Solubilities calculated from Knox's data ($K_3 = 10^{-15}$, $K_4 = 10^{-7}$, $K_1/K_2 = 14$) directly are given in columns 3 and 5.

No way has been found to reconcile all the experimental data of Knox, Kubli and Saukov with any set of values of K_1, K_2, K_3 and K_4. For present purposes this is not critical, since as Table I shows, the calculated solubilities of HgS are not very sensitive to particular values of the equilibrium constants —provided the constants used are consistent among themselves.

TABLE I.

MERCURY DISSOLVED BY EXCESS SULFIDE ION AT 25° C.

pH	Dissolved HgS if total dissolved S is 0.1 mole/liter		Dissolved HgS if total dissolved S is 0.001 mole/liter	
	Knox + Kubli + Saukov (mole/liter)	Knox (mole/liter)	Knox + Kubli + Saukov (mole/liter)	Knox (mole/liter)
1	1.5×10^{-20}	1.4×10^{-20}	1.5×10^{-22}	1.4×10^{-22}
4	1.5×10^{-14}	1.4×10^{-14}	1.5×10^{-16}	1.4×10^{-16}
7	7.5×10^{-9}	7.0×10^{-9}	7.5×10^{-11}	7.0×10^{-11}
10	1.5×10^{-6}	1.4×10^{-6}	1.5×10^{-7}	1.4×10^{-7}
13	0.007	0.012	7×10^{-5}	1.2×10^{-4}

The numbers in Table I mean that at 25° C a neutral solution containing 0.1 mole/liter of dissolved sulfur (chiefly as HS^-) is capable of holding in solution 7×10^{-9} mole/liter, or 1.4×10^{-6} gram/liter, of mercury, an amount well above the lower limit we have adopted for a reasonable concentration in vein solutions. If the total dissolved sulfur is 0.001 mole/liter, a slight alkalinity (pH = about 8.5) would dissolve the same amount. Evidently sulfide solutions are adequate to transport mercury at low temperatures, even when the pH is near 7.

At high temperatures solubilities of HgS in alkaline sulfide solutions are smaller. This is evident from Knox's statement that the solubility is slightly less at 33° C than at 25°, from Saukov's comparison of solubilities at 17° and 57°, and from Treadwell and Schaufelberger's (9) observation that heat is evolved when HgS is added to a solution of S^{--}. Saukov's results show a decrease of 25% in solubility for a 40-degree rise in temperature. This rate of decrease cannot safely be extrapolated to higher temperatures, but at least it indicates that solubilities in the neighborhood of 300° can hardly be as small as 1/100 of those given in Table I. This would still

permit the transportation of appreciable amounts of mercury by slightly basic solutions of sulfide ion. Possible methods of precipitation of HgS from such solutions have been discussed by Dreyer(1).

THIRD MECHANISM: SULFOMERCURIC ACID.

A possible variant of the alkaline sulfide hypothesis is provided by recent work of Treadwell and Schaufelberger (9), whose data unfortunately disagree with those of Knox (7) and Saukov (13).

Treadwell and Schaufelberger's chief interest was in determining some of the thermodynamic properties of HgS by measuring equilibria in its reaction with hydrogen. To provide an independent check on some of their work they made a single measurement of the solubility of HgS in a solution of 1*N* perchloric acid saturated with H_2S, obtaining the unexpectedly high value of 3.3×10^{-7} mole/liter at 18° C. To account for this high solubility they postulate the existence in solution of a compound H_2HgS_2, the acid corresponding to the complex sulfide ion HgS_2^{--}. In order to get some idea of the properties of such a compound, the authors made a rough measurement of the heat evolved when HgS is dissolved in Na_2S solution, obtaining a figure of 9,400 cal/mole. In the absence of any data on the entropy of H_2HgS_2 or its ions, they assume that this figure may be used also as the free energy of the reaction

$$HgS + S^{--} = HgS_2^{--}.$$

The free energy of the reaction

$$HgS = Hg^{++} + S^{--}$$

can be obtained from the solubility product.

$$(\Delta F = - RT \ln K = - RT \ln (Hg^{++})(S^{--})),$$

and by subtracting the first equation from the second the free energy and equilibrium constant can be found for

$$HgS_2^{--} = Hg^{++} + 2S^{--}.$$

The results are 78,700 cal/mole for the free energy, and 4×10^{-60} for the constant at 18° C. If this figure and the solubility product of cinnabar are used in a calculation like that of the last section, the ratio K_1/K_2 becomes $7 \times 10^{-53}/4 \times 10^{-60}$ or 1.8×10^{7}, instead of the value 0.15 based on Knox's and Saukov's data. So high a value makes this ratio the controlling factor in S^{--} concentration for all values of pH above 7, and leads to the hardly credible result that HgS is soluble to the extent of nearly half the total dissolved sulfur for any solution on the alkaline side of neutral.

In order to make this calculation precisely, it is necessary to add two more equations to the list on pages 501 and 502:

$$H_2HgS_2 = H^+ + HHgS_2^- \quad (7)$$

$$HHgS_2^- = H^+ + HgS_2^{--} \quad (8)$$

with the corresponding equilibrium constants

$$\frac{(HHgS_2^-)\,(H^+)}{(H_2HgS_2)} = K_5 \qquad \frac{(HgS_2^{--})\,(H^+)}{(HHgS_2^-)} = K_6.$$

From Treadwell and Schaufelberger's work it is not possible to find K_5 and K_6 individually, but the product K_5K_6 can be calculated as about 10^{-7}. In making the calculations of solubility of HgS some assumption must be made about the individual values, but no conceivable pair giving this product changes the obvious absurdity of the computed solubilities.

One other indication that something is wrong with Treadwell and Schaufelberger's measurement of heat of reaction is obtained from Saukov's data on the change of solubility of HgS with temperature. Saukov gives for the solubility in 0.05 *M* Na_2S:

0.02236 g/50 cm³ at 17° C.
0.01680 g/50 cm³ at 57° C.

These are equivalent to 0.00192 mole/liter and 0.00145 mole/liter, respectively. The reaction and equilibrium constant are

$$HgS + S^{--} = HgS_2^{--};\ K = \frac{(HgS_2^{--})}{(S^{--})}.$$

As an approximation we can assume (S^{--}) to be the same at the two temperatures, so that $K = (HgS_2^{--})/\text{const.}$ In the integrated form of the Van't Hoff equation,

$$\ln K = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + C,$$

the constant (S^{--}) becomes part of the integration constant C; (HgS_2^{--}) can be used for K, T = 290 and 330, R = 1.98 cal. Then for the two temperatures,

$$\ln 0.00192 = -\frac{\Delta H}{1.98}\left(\frac{1}{290}\right) + C$$

$$\ln 0.00145 = -\frac{\Delta H}{1.98}\left(\frac{1}{330}\right) + C$$

C can be eliminated by subtraction, and ΔH turns out to be $-$ 1,370 cal/mole, which is very different from Treadwell and Schaufelberger's figure, $-$ 9,400 cal/mole.

In view of these discrepancies it seemed best to disregard all calculations based on the heat of reaction. It appeared possible, however, that by working backward, accepting Treadwell and Schaufelberger's solubility measurement in acid and the data of Knox and Saukov in alkali, some more reasonable figures might be obtained for the ionization constants of H_2HgS_2 and for the ratio K_1/K_2. In order to carry this out it was assumed that the ratio K_5/K_6 is 10^5, since this is the common ratio of the ionization constants of diprotic oxygen acids; a change in this ratio by two or three powers of ten

would not greatly affect the results. The procedure in calculation was the same as before: equations (1), (2), (3), (4), (7) and (8), plus the additional relation that

$$(HS^-)+(H_2S)+(2HgS_2^{--})+(2HHgS_2^-)+(2H_2HgS_2)+(S^{--})=\text{total S}$$

give seven equations in seven unknowns for any pair of values of total S and H^+. The solutions of the equations this time, however, will not be numbers but algebraic expressions involving K_6 and the ratio K_1/K_2. For the two sets of conditions (a) pH = 1 and total S = 0.1 (Treadwell and Schaufelberger) and (b) pH = 13 and total S = 0.1 (Knox and Saukov), solubilities of HgS are known experimentally. Hence for these sets of conditions the algebraic expressions involving K_1/K_2 and K_6 can be set equal to numbers. Then the problem is reduced to two equations in two unknowns, which are readily soluble. Actually the calculation is less formidable than it sounds, because in any given set of conditions some of the numerous variables are negligibly small with respect to others.

From this calculation K_1/K_2 is 0.24 and K_6 is 1.5×10^{-10}. If we accept Treadwell and Schaufelberger's value 7×10^{-53} for K_1 and if we assume that $K_5 = 10^5 K_6$, it follows that K_2 is 2.9×10^{-52} and K_5 is 1.5×10^{-5}. With these figures we have everything necessary to calculate the solubility of HgS for any values of pH and total S. The results for solutions with total S = 0.1 mole/liter are shown in Table II.

TABLE II.

SOLUBILITIES OF HgS IN SOLUTIONS WITH TOTAL DISSOLVED S = 0.1 MOLE/LITER.

pH	Solubility of HgS (moles/liter)
1	3×10^{-7}
4	3×10^{-7}
7	1×10^{-6}
10	1×10^{-4}
13	1×10^{-3}

These figures, apparently based solidly on experimental evidence, imply that the transportation of mercury in solution should be no problem at all, regardless of pH, provided only that sufficient total sulfur is dissolved to hold the mercury either as HgS_2^{--}, $HHgS_2^-$, or H_2HgS_2. The first of these substances should predominate in alkaline solutions, the second in neutral solutions, and the third in acid solutions. In neutral and acid solutions the requisite condition is the presence of dissolved H_2S, and the escape of H_2S on release of pressure would offer a convenient means of precipitating HgS. The effect of high temperature on the various equilibria is not predictable from available data, but the calculated solubilities are high enough so that they could be reduced by two or three powers of ten without making the amount of dissolved mercury unreasonably small.

These results are open to criticism on at least two grounds. First, the suggested solubilities in neutral solutions saturated with H_2S are high enough to be detectable in simple qualitative tests; such experiments carried out by the writer failed to show any detectable solubility until the pH was

high enough to make appreciable the formation of HgS_2^{--} in the manner postulated by Knox (7). Second, from the value of K_2 obtained above the free energy of the reaction

$$HgS + S^{--} = HgS_2^{--}$$

can be calculated as 800 cal/mole, a figure much too small in comparison with the experimentally determined heat of reaction, − 9,400 cal/mole. It looks as if Treadwell and Schaufelberger's data are somewhere inconsistent, either among themselves or with Knox's and Saukov's data on solubility in alkaline sulfide solutions.

The whole question of the solubility of HgS in acid is in a most unsatisfactory state. Dorenfeldt-Holtan (15) and Broderick (16), in addition to Treadwell and Schaufelberger, claim to have experimental evidence for slight solubility in acid; these authors, furthermore, do not find H_2S necessary to aid solubility. Such results are hard to reconcile with ordinary analytical procedure, in which mercury is quantitatively separated from other elements by virtue of the extreme insolubility of its sulfide in acid. Dorenfeldt-Holtan and Kolthoff (8) suggest that the apparent solubility of HgS depends strongly on the particle size; Kolthoff suggests further that the solubility apparently changes with time because of slow particle growth. Another possibility is suggested by the work of Linder and Picton (17), who report that HgS under certain conditions will disperse itself as a colloid (up to 10 mg/liter) in water saturated with H_2S.

In summary, there seems to be little clear evidence that sulfide solutions with pH less than 7 can transport significant amounts of mercury, except possibly as a colloid. In particular, the evidence for the existence of the acid H_2HgS_2 seems very shaky.

FOURTH MECHANISM: COMPLEX CHLORIDE IONS.

Mercury forms a variety of complex ions with the halogens. Discussion here will be limited to the complexes of divalent mercury and chlorine, since these are the substances most likely to be present in considerable amounts in ore solutions. For the complexes present in a solution of a mercuric salt in excess Cl^-, Luther (18) lists $HgCl_2$, $HgCl^+$, Hg_2Cl_2O, and $HgCl_4^{--}$. Lindgren, Johnson and Sillén (19) consider the important substances to be $HgCl_2$, $HgCl_3^-$ and $HgCl_4^{--}$. There is general agreement that the most stable of these complexes is $HgCl_4^{--}$; for the reaction

$$Hg^{++} + 4Cl^- = HgCl_4^{--}$$

the equilibrium constant ($K_7 = (HgCl_4^{--})/(Hg^{++})(Cl^-)^4$) at 25° C is calculated by Sherrill (20) to be 9×10^{15} and by Lindgren, Johnson and Sillén to be 1.2×10^{15}. The important question from the standpoint of ore deposits is whether the complex is sufficiently stable so that HgS might be soluble in excess Cl^-. In other words, in the reaction

$$HgS + 4Cl^- = HgCl_4^{--} + S^{--} \qquad (9)$$

will excess Cl^- force the equilibrium appreciably to the right?

The equilibrium constant for this reaction is the product of the constants for equations (1) and (9), since

$$\frac{(HgCl_4^{--})}{(Hg^{++})\,(Cl^-)^4} \times (Hg^{++})\,(S^{--}) = K_7K_1 = \frac{(HgCl_4^{--})\,(S^{--})}{(Cl^-)^4}.$$

If we use the value of K_1 given by Treadwell and Schaufelberger (9) for metacinnabar, and the value of K_7 given by Sherrill (since these are the highest reported values with some degree of reliability), the product K_1K_7 is $0.3 \times 10^{-51} \times 9 \times 10^{15}$ or 2.7×10^{-36}. If we assume a 4 *M* solution of Cl^- (the highest concentration of Cl^- reported by Newhouse (21) in fluid inclusions in vein minerals),

$$(HgCl_4^{--})\,(S^{--}) = (Cl^-)^4 \times 2.7 \times 10^{-36} = 4^4 \times 2.7 \times 10^{-36} = 6.9 \times 10^{-34}.$$

If nothing else influences the concentrations of $HgCl_4^{--}$ and S^{--}, the concentration of each would be the square root of this figure, or 2.6×10^{-17} mole/liter, an amount far too small to have any appreciable effect in mercury transportation.

If the solution is acid as well as rich in Cl^-, the formation of H_2S will increase the solubility of HgS:

$$HgS + 4Cl^- + 2H^+ = HgCl_4^{--} + H_2S.$$

The equilibrium constant for this reaction is

$$K = \frac{(HgCl_4^{--}) \cdot (H_2S)}{(Cl^-)^4 \cdot (H^+)^2} = \frac{(HgCl_4^{--})}{(Hg^{++})\,(Cl^-)^4} \cdot (Hg^{++})\,(S^{--}) \cdot \frac{(H_2S)}{(S^{--})\,(H^+)^2}$$

$$= \frac{K_7 \times K_1}{K_3 \times K_4} = \frac{2.7 \times 10^{-36}}{10^{-13} \times 10^{-7}} = 2.7 \times 10^{-16}.$$

In a solution containing 4 *M* Cl^- and 1 *M* H^+,

$$(HgCl_4^{--})\,(H_2S) = 2.7 \times 10^{-16} \times 4^4 \times 1^2 = 6.9 \times 10^{-14}$$

and if no additional H_2S is present,

$$HgCl_4^{--} = 2.6 \times 10^{-7} \text{ mole/liter.}$$

A similar calculation has been carried through by Korenman (22); using different values of the fundamental constants, he obtains a somewhat higher value of K, 1.5×10^{-15}, giving a solubility in 4 *M* Cl^- and 1 *M* H^+ of 6.2×10^{-7} mole/liter.

Under the most favorable conditions of high Cl^-, high H^+ and low H_2S, conditions that would seldom or never be reached in nature, the solubility of HgS is thus barely high enough to be significant. Conceivably an increase in temperature might raise the solubility somewhat; no data have been found on the effect of temperature, but an increase in solubility of more than 100-fold is unlikely in a temperature range of 200°. Except under extreme conditions this would not help appreciably in the transportation of mercury.

Since the chloride complexes are inadequate for transporting mercury in

the presence of sulfur, and since other complex-forming elements are scarce in vein solutions, it seems safe to conclude that no complex ion except HgS_2^{--} is likely to play a role in the formation of quicksilver ores.

FIFTH MECHANISM: IONIZATION OF HYDROGEN SULFIDE.

Conceivably the ionization of dissolved hydrogen sulfide at high temperatures might be so small that the concentration of S^{--} would be insufficient to precipitate HgS. This suggestion is proved impossible by the positive values of the heats of reaction for the dissociation processes ($H_2S = H^+ + HS^-$, $\Delta H = 6{,}000$ cal/mole; $HS^- = H^+ + S^{--}$, $\Delta H = +3{,}869$ cal/mole; from Lewis and Randall (23)). By Van't Hoff's law $d \ln K/dT = \Delta H/RT^2$, which means that for positive values of ΔH, K must increase with a rise in temperature. Hence both steps in the ionization of H_2S would increase rather than decrease, and the concentration of S^{--} (for a given concentration of H_2S) would be greater at high temperatures rather than less. Numerical values of the dissociation constants for temperatures up to 400°, calculated from the integrated form of Van't Hoff's law on the assumption that the ΔH's are constant, can be found in Verhoogen's (11) paper; experimental work by Wright and Maass (24) in the range 5–60° C demonstrates that the actual increase in the dissociation constants is much greater than Verhoogen's calculations indicate. Provided dissolved H_2S is present, there will be no lack of S^{--} to unite with mercury at high temperatures.

SIXTH MECHANISM: SOLUBILITY OF HYDROGEN SULFIDE.

It is possible that mercury can be held in solution at high temperatures because the solubility of H_2S becomes negligible. This is a more difficult problem to handle, since the solubility depends strongly on partial pressure as well as temperature, and partial pressures in vein fluids can only be guessed. Another difficulty is lack of basic solubility data for temperatures over 100° C.

Solubility data for the range 0–100° are given in the Handbook of Chemistry and Physics (25). These data are given as volumes of gas (reduced to 0° C and atmospheric pressure) dissolved in one volume of water, when the partial pressure of the gas (regardless of the pressure of water vapor) is one atmosphere. Figure 1 is a plot of these figures; abscissae are logarithms of the solubilities and ordinates are reciprocals of the absolute temperatures. Extrapolation of such a curve to 300°, or even to 200°, is manifestly unsafe, but in the absence of other data it can be used to set limits. The most likely extrapolation, shown by the dashed line, gives a value of about -0.24 for log solubility at 300° C, or a solubility of about 0.56 vol/vol. To be sure that the extrapolation does not give too high a solubility, however, let us regard the last two points of the curve as uncertain and extrapolate from the remainder, as shown by the dotted line. To make doubly sure that the solubility will be minimized rather than exaggerated, the extrapolated line is drawn straight. This gives -0.64 for the logarithm, and 0.22 vol/vol for the solubility at 300°. In other words, a liter of water at 300° should dissolve

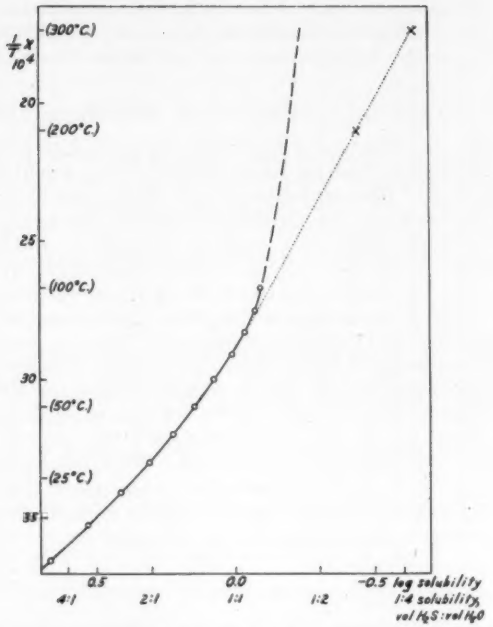

FIG. 1. Change of solubility of H_2S in H_2O with temperature.

at least 0.22 liter of H_2S, or $0.22/22.4 = 0.01$ mole, since the 0.22 liter is measured at standard conditions. This is about one-tenth of the solubility at 25° C, and the extent of ionization is greater, so that the amount of S^{--} should be ample to precipitate mercury from solution.

SEVENTH MECHANISM: REACTION OF HYDROGEN SULFIDE WITH GASES.

The preceding discussion assumes that the partial pressure of H_2S in equilibrium with the ore solution is unaffected by reactions in the gas phase. If, on the other hand, we assume that the solution is accompanied at all times by gas, and assume further that reactions in the gas keep the concentration of H_2S very low at 300° but release more and more as the temperature falls, we have another possible mechanism of mercury deposition. Butler (26), basing his ideas on a suggestion by Zies, has used this hypothesis as an explanation for sulfide veins in general. The two reactions proposed by Zies for the control of H_2S partial pressure are

$$2H_2O + H_2S = 3H_2 + SO_2, ,$$
$$2H_2O + 3S = 2H_2S + SO_2.$$

The first reaction is known (Randall and Bichowsky, 27) to be displaced to the right at high temperatures, and it is Butler's idea that at temperatures over 200° C it will keep the pressure of H_2S vanishingly small.

Thermodynamic data permitting the accurate computation of free energies at various temperatures for these reactions and for others involving hydrogen and the sulfur gases have been collected by Kelley (28) and Rossini (29). The resulting free energies and corresponding equilibrium constants are shown in Table III. As an example of the calculations: for the reaction between H_2O and H_2S at 127° C the free energy of formation of H_2O at 127° is given in Rossini's tables as − 53,516 cal/mole; the free energy of formation of H_2S is calculated by substituting in the formula given by Kelley

$$2H_2 + S_2(g) = 2H_2S(g)$$

$$\begin{aligned}\Delta F^\circ &= -38{,}810 + 15.41T \log T - 2.065 \times 10^{-3}T^2 - 25.02T \\ &= -38{,}810 + 15.41 \times 400 \times \log 400 - 2.065 \times 10^{-3} \times 400^2 \\ &\qquad - 25.02 \times 400 \\ &\quad - 33{,}160 \text{ cal for 2 moles}\end{aligned}$$

and the free energy of SO_2 is obtained from another formula of Kelley's:

$$S_2(g) + 2O_2 = 2SO_2$$

$$\begin{aligned}\Delta F^\circ &= -172{,}630 + 3.43T \log T - 0.712 \times 10^{-3}T^2 + 0.168 \times 10^5 T^{-1} \\ &\qquad + 24.30T \\ &= -159{,}480 \text{ cal for 2 moles.}\end{aligned}$$

The free energy of formation of H_2 is zero by convention. Then for the reaction

$$2H_2O + H_2S = 3H_2 + SO_2$$

$$\begin{aligned}\Delta F^\circ &= \Delta F^\circ(SO_2) - 2\Delta F^\circ(H_2O) - \Delta F^\circ(H_2S), \\ &= -\tfrac{1}{2} \times 159{,}480 + 2 \times 53{,}516 + \tfrac{1}{2} \times 33{,}160, \\ &= +43{,}872 \text{ cal/mole.}\end{aligned}$$

The equilibrium constant is calculated from the relation

$$\begin{aligned}\Delta F^\circ &= -RT \ln K, \\ 43{,}872 &= -1.987 \times 400 \times 2.303 \times \log K, \\ \log K &= -24.00, \\ K &= 10^{-24}.\end{aligned}$$

Of the reactions involving H_2S in Table III, reaction (1) is indeed displaced toward H_2S with falling temperature, but the low values of K show that it is not displaced appreciably in the other direction at any temperature under 1,100° K (for example, in an equilibrium mixture at 1,160° Randall and Bichowsky (27) find that the ratio of H_2S to H_2 is still 10:1). Surely this reaction can be of no help in keeping mercury in solution at 300°C. Reaction (2) is displaced to the left, i.e., in a direction to use up H_2S rather than to form it, as the temperature falls. At 600–700° C the four gases in this reaction could exist together in roughly equal amounts; as the temperature falls more and more H_2S and SO_2 will react to form sulfur and water.

TABLE III.

FREE ENERGIES AND EQUILIBRIUM CONSTANTS FOR REACTIONS INVOLVING THE SULFUR GASES AND HYDROGEN.

Temperature, degrees centigrade. Temperature, degrees absolute...	25 298.1	127 400	227 500	427 700	627 900	
1) $2H_2O + H_2S = 3H_2 + SO_2$	+45,383 −33.26	+43,872 −24.00	+42,248 −18.46	+38,641 −12.06	+34,695 −8.43	ΔF°, cal/mole log K
2) $2H_2O + \frac{3}{2}S_2 = 2H_2S + SO_2$	+17,006 −12.46	+14,205 −7.75	+11,528 −5.04	+6,073 −1.90	+849 −0.21	ΔF°, cal/mole log K
3) $CO_2 + H_2S = H_2O + CO + \frac{1}{2}S_2$	+16,276 −11.94	+15,691 −8.56	+15,090 −6.59	+13,915 −4.35	+12,695 −3.08	ΔF°, cal/mole log K
4) $SO_2 + CH_4 = H_2S + CO + H_2O$	−11,416 +8.37	−15,315 +8.37	−19,233 +8.43	−27,205 +8.43	−35,170 +8.51	ΔF°, cal/mole log K
5) $CO_2 + 2H_2S = CH_4 + SO_2 + \frac{3}{2}S_2$	+27,692 −20.3	+31,006 −16.95	+34,323 −15.00	+41,120 −12.85	+47,870 −11.64	ΔF°, cal/mole log K
6) $3CO_2 + H_2S = H_2O + 3CO + SO_2$	+65,834 −48.3				+38,934 −9.71	ΔF°, cal/mole log K
7) $CH_4 + 3CO_2 = 4CO + 2H_2O$	+54,418 −39.9	+45,963 −25.1	+37,565 −16.41	+20,589 −6.43	+3,762 −0.91	ΔF°, cal/mole log K
8) $CH_4 + H_2O = 3H_2 + CO$	+33,967 −24.9	+28,557 −15.58	+23,015 −10.06	+11,436 −3.57	−480 +0.12	ΔF°, cal/mole log K
9) $H_2O + CO = CO_2 + H_2$	−6,817 +4.99	−5,802 +3.17	−4,850 +2.12	−3,059 +0.95	−1,413 +0.34	ΔF°, cal/mole log K
10) $2CO + SO_2 = 2CO_2 + \frac{1}{2}S_2$	−49,558 +36.32	−45,587 +24.90	−41,708 +18.21	−33,903 +10.59	−26,239 +6.37	ΔF°, cal/mole log K
11) $2NH_3 + SO_2 = H_2S + N_2 + 2H_2O$	−37,560 +27.6	−41,070 +22.5	−44,450 +19.4	−51,840 +16.2	−58,900 +14.3	ΔF°, cal/mole log K

Note: Free sulfur is indicated in all reactions by S_8. At higher temperatures S_6 and S_2 become increasingly important, but neglect of these substances does not greatly affect the free energies.

In other words, if excess SO_2 remains after reacting with H_2 according to equation (1), it will progressively remove H_2S as the temperature is lowered according to reaction (2). Reactions (3), (5), (6) and (11), like reaction (1), would be displaced in a direction to increase the amount of H_2S as the temperature falls; but all four, again like equation (1), are displaced so far in the direction of H_2S even at temperatures above 600° C that they could not possibly reduce its concentration sufficiently to permit solution of HgS. The equilibrium constant for reaction (4) remains practically unchanged over the temperature range 25–627° C and throughout this range H_2S is favored over SO_2.

A more quantitative discussion of these equilibria seems futile, since initial concentrations of the various gases are not known and since the attainment of equilibrium in such systems is slow (Shepherd (30)). One odd deduction, however, is worth mentioning: at any temperature in this range SO_2 should be unstable with respect to H_2S—a conclusion which seems to

contradict the often-reported preponderance of SO_2 in high-temperature fumaroles and of H_2S in low-temperature fumaroles. The reactions here considered do not include oxidizing agents like free O_2 and Cl_2, which of course would make SO_2 more stable; it may be that their presence in the original gases, or the addition of oxygen from the air, is sufficient to account for SO_2 in high-temperature fumaroles. One might speculate that such oxidation reactions could eliminate H_2S at higher temperatures, thus permitting mercury to dissolve; but most reported analyses of volcanic gases show insufficient Cl_2 to react even with all the free hydrogen, and if enough atmospheric oxygen were added to oxidize H_2S quantitatively its presence should be revealed in other more conspicuous oxidation effects.

Figures like those in Table III are of little help in predicting just what gases will be present in any given situation, but they do demonstrate the negative conclusion that no conceivable equilibrium or combination of equilibria among the ordinary fumarolic gases can account for the deposition of HgS by suppressing H_2S at high temperatures and releasing it at low temperatures.

EIGHTH MECHANISM: VOLATILITY OF MERCURIC CHLORIDE.

If mercuric chloride is sufficiently volatile, and in the vapor phase sufficiently stable with respect to HgS, mercury could be transported in this form and then precipitated as the sulfide when the vapor condenses.

Data on the volatility of $HgCl_2$ are given by Kelley (31):

Temperature, ° C	Vapor pressure, atmos.
96	0.0001
131	0.001
174	0.01
228	0.1
254	0.25
273	0.5
304	1.0

At 300° C $HgCl_2$ has a vapor pressure of nearly one atmosphere, and at 200° almost 1/10 of an amtosphere. It is evident that volatile transfer of this compound is possible at the temperatures of formation of quicksilver ores.

In a gas containing H_2S, however, such a mechanism will be possible only if the equilibrium

$$HgCl_2(g) + H_2S(g) = HgS(s) + 2HCl(g) \qquad (8)$$

is not displaced far to the right. To locate the positions of equilibrium in this reaction it is necessary to know the free energies of formation of HgS(s), HCl(g) and $HgCl_2$(g) at various temperatures, as well as the free energies for H_2S(g) used in the last section. For HCl, the International Critical Tables (32) give the equation

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 = HCl$$
$$\Delta F^\circ = -21{,}870 + 0.45T \ln T - 0.000025T^2 - 5.31T.$$

For HgS, Kelley (28) gives

$$2HgS(s) = 2Hg(g) + S_2(g)$$
$$\Delta F^\circ = 92{,}700 + 9.49T \log T + 3.20 \times 10^{-3}T^2 - 136.71T.$$

The accuracy of this equation will be discussed in the next section; for present purposes an error of even several thousand calories would be immaterial. For $HgCl_2(g)$ the problem is slightly more complicated. The International Critical Tables give $\Delta H_{298} = -36{,}658$, $\Delta F^\circ_{298} = -34{,}569$, and $\Delta S_{298} = -7.0$, for the reaction

$$Hg(1) + Cl_2(g) = HgCl_2(g).$$

For each of these three substances Kelley (33) gives the change in heat content ($H_T - H_{298}$) and change in entropy ($S_T - S_{298}$) for various temperatures. If we take 127° C (400° K.) as an example,

	Hg(1)	$Cl_2(g)$	$HgCl_2(g)$
$H_{400} - H_{298}$	673	840	1,435
$S_{400} - S_{298}$	1.94	2.42	4.14

This means that the negative value of ΔH for the reaction is increased by 1,435 − 673 − 840 or 78 cal/mole as the temperature rises from 25 to 127° C, and that the negative value of ΔS is increased by 4.14 − 1.94 − 2.42 or 0.22 cal/mole/degree. Hence

$$\Delta F^\circ_{400} = \Delta H_{400} - T\Delta S_{400},$$
$$= (-36{,}658 - 78) - 400\,(-7.0 - 0.22),$$
$$-33{,}858 \text{ cal/mole.}$$

After values of ΔF° are calculated in this manner, it is necessary to subtract from them free energy changes for the reaction

$$Hg(1) = Hg(g)$$

for which Kelley gives

$$\Delta F^\circ = 15{,}024 + 3.78 \log T - 34.29T.$$

Combination of the free energies of formation gives for reaction (8):

Temperature, ° C	ΔF°	log K
127	−14,360	+7.87
227	−13,570	+5.94
627	−10,500	+2.55

Thus the reaction is displaced in the direction of HgS for temperatures well over the range which is of importance in cinnabar deposition. The values of log K are small enough, however, so that pressures of $HgCl_2$ in equilibrium with HgS may under some conditions be appreciable. Table IV shows equilibrium pressures calculated for various combinations of HCl and H_2S which might reasonably be expected in an ore-forming vapor.
(Perhaps an example will help to give these figures meaning. In a gas at 0° C in which $HgCl_2$ exerts a partial pressure of 10^{-5} atmospheres, every liter would contain $200.6 \times 10^{-5}/22.4 = 0.0001$ grams of mercury.)

TABLE IV.

VAPOR PRESSURES OF $HgCl_2$ AT VARIOUS CONCENTRATIONS OF HCl AND H_2S.

Temperature, ° C	HCl, atmos	H_2S, atmos	$HgCl_2$, atmos
127	1	1	$10^{-7.0}$
127	1	0.001	$10^{-4.0}$
127	0.01	0.001	$10^{-6.0}$
227	1	1	$10^{-5.0}$
227	1	0.001	$10^{-2.0}$
227	0.01	0.001	$10^{-4.0}$
627	1	1	$10^{-2.6}$
627	1	0.001	$10^{+0.4}$
627	0.01	0.001	$10^{-3.6}$

Table IV indicates that significant amounts of mercury can be transported as $HgCl_2$ vapor even in the presence of H_2S, the amounts decreasing as the temperature falls and as the HCl/H_2S ratio becomes smaller. It should be emphasized, however, that if a liquid phase is present the HCl/H_2S ratio in the vapor will necessarily be low because of the extreme solubility of HCl; so this method of transportation of mercury will be most effective if the vein fluid consists of vapor only.

NINTH MECHANISM: THERMAL INSTABILITY OF MERCURIC SULFIDE.

The opinion of Allen and Crenshaw (34) that mercuric sulfide is stable at all temperatures up to its (apparent) sublimation point (580° C) has been widely quoted (for instance, Dreyer (1) and Brown (35)). Allen and Crenshaw, however, based their view simply on the facts that vapor in equilibrium with solid HgS reaches atmospheric pressure at about 580°, and that the vapor condenses to HgS on cooling, without inquiring into the nature of the vapor. Rinse (10), on the other hand, gives evidence that HgS vapor is completely dissociated into its elements at temperatures at least as low as 300° C, his evidence consisting of the fact that measured vapor pressures agree with those calculated for complete dissociation, and the fact that addition of either pure mercury or sulfur lowers the vapor pressure according to the mass action law. He finds that even at 100° precipitated HgS cannot be freed from excess sulfur by heating, because the precipitate slowly decomposes and hence acquires an excess of mercury over sulfur. A similar conclusion follows from the failure of Iredale and Gibson (36) to find any absorption spectrum which they could ascribe to HgS molecules in the vapor in equilibrium with HgS at 400°; this result, however, is disputed by Sen-Gupta (37). The thermodynamic data for the dissociation of HgS are not in good agreement, but all sets of data indicate that the compound should decompose at least to some extent in the temperature range important in ore deposition.

Kelley (28) discusses in great detail the thermodynamic data available up to 1937, making tentative calculations on the basis of Rinse's measurements but pointing out that the results disagree with other work. As a

tentative equation for the free energy of the reaction

$$2HgS(red) = 2Hg(g) + S_2(g),$$

Kelley gives

$$\Delta F^\circ = 92{,}700 + 9.49 \log T + 3.20 \times 10^{-3}T^2 - 136.71T,$$

from which the following values of the free energies and equilibrium constants are obtained:

Temperature, ° C	ΔF°	log K
27	59,000	−43.15
127	48,400	−26.52
227	37,900	−16.61
327	27,700	−10.11

If we assume that all the sulfur vapor is S_2, and that no mercury or sulfur vapor is present except that from the decomposition of HgS, we can write $(Hg) = 2(S_2)$ and

$$K = (Hg)^2(S_2) = (2S_2)^2(S_2) = 4(S_2)^3,$$

or

$$(S_2) = \tfrac{1}{2}(Hg) = \sqrt[3]{K/4}.$$

Values for the equilibrium pressures of S_2 and Hg calculated in this way are shown in the second and third columns of Table V. Columns four and five show similar figures based on the assumption that all the sulfur vapor is S_8. Actually the sulfur is a mixture of S_2, S_6, and S_8, the proportions varying with temperature; since the figures in the table for the limiting cases of pure S_2 and pure S_8 do not differ by as much as a factor of 3, consideration of the complicated sulfur vapor equilibrium is not important for present purposes.

Kelley makes clear that the thermodynamic data on which Table V is based are of doubtful reliability. For one thing they lead to values of $\Delta H_{298} = -15{,}550$ and $\Delta F^\circ_{298} = -12{,}340$ cal/mole for the formation of HgS from liquid mercury and rhombic sulfur; these in turn give 15.3 cal/mole/degree for the entropy of HgS, which Kelley feels is too low in comparison with known entropies of the mercury oxides. Furthermore, the figure for free energy of formation leads (by adding free energy changes for the reactions $Hg = Hg^{++} + 2e^-$ and $S + 2e^- = S^{--}$, calculated from stand-

TABLE V.

PRESSURES OF MERCURY VAPOR AND SULFUR VAPOR IN EQUILIBRIUM WITH HgS BASED ON KELLEY'S CALCULATIONS FROM THE DATA OF RINSE.

Temperature, °C	All S calculated as S_2		All S calculated as S_8	
	S_2, atmos	Hg, atmos	S_8, atmos	Hg, atmos
27	2.6×10^{-15}	5.2×10^{-15}	1.7×10^{-15}	1.4×10^{-14}
127	9.1×10^{-10}	1.8×10^{-9}	4.7×10^{-10}	3.8×10^{-9}
227	1.8×10^{-6}	3.6×10^{-6}	8.3×10^{-7}	6.6×10^{-6}
327	2.9×10^{-4}	5.8×10^{-4}	1.2×10^{-4}	9.4×10^{-4}

ard electrode potentials) to the value 75,200 for $\Delta F°_{298}$ for the reaction $HgS = Hg^{++} + S^{--}$, and this in turn gives a solubility product of 10^{-55}—lower by a factor of 30 than any other found in the literature. Because of these discrepancies it is important to explore other sets of thermodynamic data, although from no other sets can the vapor pressures be obtained as directly as from Rinse's work.

Other reported figures for the heat and free energy of formation are as follows:

ΔH_{298}:	−6,210	Landolt-Börnstein, Physikalisch-chemische Tabellen, 1923 (Thomsen) (38)
	−10,900	Ibid. (Varet) (38)
	−10,700	Bichowsky and Rossini, 1936 (39)
	−14,470	Makolkin, 1942 (40)
Δ(cinnabar)	−14,000	Treadwell and Schaufelberger, 1946 (9)
Δ(metacinnabar)	−13,800	
$\Delta F°_{298}$:	−10,330	Calculated by Kelley (28) from Knox's (7) value of the solubility product, 3×10^{-54} (1906)
	−10,470	Makolkin, 1942 (40)
	−8,800	Latimer 1938 (41)

The most recent measurements are those of Treadwell and Schaufelberger. From their value of the solubility product of cinnabar, 7×10^{-53}, the free energy change of solution is 69,300 cal; and by adding to this free energies corresponding to electrode potentials of the mercury and sulfur half-cells we obtain − 6,480 cal/mole as the free energy of formation of HgS from liquid mercury and rhombic sulfur.[2] By adding free energies for the reactions $2S = S_2(g)$ and $Hg(1) = Hg(g)$ (both given by Kelley), we obtain 47,500 cal/mole as $\Delta F°_{298}$ for the reaction

$$2HgS(s) = 2Hg(g) + S_2(g).$$

For this same reaction we obtain $\Delta H_{298} = 88{,}090$ cal/mole by adding to Treadwell and Schaufelberger's figure, 14,000, the ΔH's given by Kelley for $2S = S_2(g)$ and $Hg(1) = Hg(g)$.

Now to find the effect of temperature, we must modify the equations used by Kelley to fit these new values of $\Delta F°_{298}$ and ΔH_{298}. Starting with Kelley's equation for the change in heat capacity for the reaction $2HgS = 2Hg(g) + S_2(g)$,

$$C_p = -4.12 - 6.41 \times 10^{-3}T$$

we obtain by integration

$$\Delta H = \int \Delta C_p dT = \Delta H_0 - 4.12T - 3.20 \times 10^{-3}T^2.$$

Kelley evaluates the integration constant ΔH_0 by making a graph of Rinse's vapor pressure measurements. We can obtain it from Treadwell and Schaufelberger's data by substituting in the last equation the value of ΔH_{298} derived above:

$$\Delta H_{298} = 88{,}090 = \Delta H_0 - 4.12 \times 298 - 3.20 \times 10^{-3} \times 298^2.$$

[2] An error is introduced here by the fact that electrode potentials are given for 25° C while Treadwell and Schaufelberger's work was done at 18° C. The error could not be greater than 1,000 cal/mole, and would not seriously affect the results.

TABLE VI.

PRESSURES OF MERCURY VAPOR AND SULFUR VAPOR IN EQUILIBRIUM WITH HgS, CALCULATED FROM THE DATA OF TREADWELL AND SCHAUFELBERGER.

Temp, ° C	$\Delta F°$	log K	S_2, atmos	Hg, atmos
25	47,500	−35.0	1.3×10^{-12}	2.6×10^{-12}
127	33,700	−18.4	4.6×10^{-7}	9.2×10^{-7}
227	20,400	−8.9	6.8×10^{-4}	13.6×10^{-4}
327	7,300	− 2.7	8.2×10^{-2}	16.4×10^{-2}

This gives for ΔH_0 a value of 89,600 cal. The free energy change is then obtained by integrating the equation for ΔH with respect to temperature:

$$d(\Delta F/T)dT = -\Delta H/T^2,$$
$$\Delta F° = \Delta H_0 + 4.12 \times T \ln T + 3.2 \times 10^{-3}T^2 - IT.$$

At 25° C ΔH_0 is 89,600 cal/mole and $\Delta F°$ is 47,500, as calculated above. These figures can be substituted in the last equation in order to evaluate the integration constant I:

$$47{,}500 = 89{,}600 + 4.12 \times 2.303 \times 298 \times \log 298 + 3.2 \times 10^{-3} \times 298^2 - I \times 298$$

from which I = 165.5. Hence the general free energy equation is

$$\Delta F° = 89{,}600 + 4.12 \times 2.303\ T \log T + 3.2 \times 10^{-3}T^2 - 165.5.$$

Values of $\Delta F°$, log K, and equilibrium pressures of Hg and S_2 vapors calculated from this equation are shown in Table VI. These figures are roughly a hundred times larger than those in Table V.

Two other apparently reliable sets of data permit similar computations: the values $\Delta F°_{298} = -8{,}800$ cal/mole and $\Delta H_{298} = -10{,}700$ cal/mole for the formation of HgS given by Bichowsky and Rossini (39) and Latimer (41); and the values $\Delta F°_{298} = -10{,}470$ cal/mole and $\Delta H_{298} = -14{,}470$ cal/mole for the same reaction given by Makolkin (40). These two sets of numbers can be handled in exactly the same way as the data of Treadwell and Schaufelberger, giving the results shown in Tables VII and VIII:

There is little basis for choosing between the four sets of results. If Kelley (28) is right in assuming that the entropy of HgS (15.3 cal/mole/degree) calculated from Rinse's data is too low in comparison with entropies of the oxides, then both the data of Treadwell and Schaufelberger and of

TABLE VII.

PRESSURES OF MERCURY VAPOR AND SULFUR VAPOR IN EQUILIBRIUM WITH HgS CALCULATED FROM THE DATA OF BICHOWSKY AND ROSSINI AND LATIMER.

Temp, ° C	$\Delta F°$	log K	S_2, atmos	Hg, atmos
25	52,100	−38.4	1.0×10^{-13}	2.0×10^{-13}
127	42,200	−23.1	1.3×10^{-8}	2.6×10^{-8}
227	32,600	−14.2	1.2×10^{-5}	2.4×10^{-5}
327	23,000	−8.5	9.3×10^{-4}	1.9×10^{-3}

TABLE VIII.

PRESSURES OF MERCURY VAPOR AND SULFUR VAPOR IN EQUILIBRIUM WITH HgS, CALCULATED FROM THE DATA OF MAKOLKIN.

Temp, ° C	$\Delta F°$	log K	S_2, atmos	Hg, atmos
25	55,480	−40.7	1.7×10^{-14}	3.4×10^{-14}
127	44,040	−24.1	0.6×10^{-8}	1.2×10^{-8}
227	32,990	−14.4	1.0×10^{-5}	2.0×10^{-5}
327	22,240	−8.1	1.3×10^{-3}	2.6×10^{-3}

Makolkin are still more in error, since the former leads to an entropy of 0.9 and the latter to an entropy of 12.7. The data of Bichowsky and Randall and Latimer give the most reasonable figure for the entropy, 19.8. Except for this criterion, the sets of data can be considered as of equal merit. In other words the vapor pressures of mercury in equilibrium with HgS are known only within a factor of about 100. Keeping in mind this uncertainty, we may write as conservative, order-of-magnitude averages from Tables V, VI, VII and VIII:

Temp, ° C	25	127	227	327
Hg, atmos	10^{-13}	2×10^{-8}	2×10^{-5}	2×10^{-3}

A vapor pressure of 2×10^{-5} atmospheres at 227° C means that 10 cubic meters of gas would contain one gram of mercury. This is roughly the same as the vapor pressure of naphthalene or camphor at 0° C, the vapor pressure of water at − 55° C, and the vapor pressure of mercury itself at room temperature. Certainly this is a small amount, but over a period of time could account for the transportation of considerable amounts of mercury at temperatures around 200° C. At higher temperatures the equilibrium pressure is ample for the transportation of mercury; in fact, even at temperatures well under 300° the vapor pressure becomes so high that no solid mercuric sulfide could exist if there was any appreciable movement of gas through the vein fissure.

Unlike transportation as the volatile chloride, transportation of the vapor of the element itself is not greatly influenced by the presence of a solution. The vapor pressure in contact with a solution would remain the same, except for a slight reduction because of formation of HgS_2^{--} if the solution is alkaline. Thus this mechanism will satisfy the temperature requirements for cinnabar deposition and at the same time makes no demands on the character of the ore-bearing fluid except that a gas phase be present. In view of the large amounts of gas commonly associated with hot springs this does not seem a drastic requirement.

Transportation of mercury as the volatile native element or the volatile chloride provides a convenient explanation for the common separation of mercuric sulfide from nearly all other sulfides: at temperatures where the other sulfides precipitate, mercuric sulfide is unstable, so that its components are forced to travel to a cooler region before the compound can form. A

possible explanation for the deposition of calomel would be the presence of both Hg and $HgCl_2$ in the vapor; on cooling, this combination would give HgS if H_2S is present, calomel if H_2S is absent.

OTHER MECHANISMS.

There are at least two other ways in which mercury might conceivably be transported in vein fluids: as a supersaturated solution of the sulfide, and as a colloidal dispersion. Unlike the nine mechanisms so far considered, these two mechanisms cannot be assessed quantitatively from presently available data.

Supersaturation implies sluggishness in the attainment of equilibrium between a solute and the precipitated solid. For the particular case of mercury sulfide, it would mean that a high-temperature solution containing the sulfide, or a solution formed by the mixing of mercury and sulfide ions from different sources, might retain the sulfide in solution down to the temperature range of cinnabar deposition, despite lack of equilibrium in the solution before deposition occurred. Since supersaturation is a metastable state, it is normally favored by relatively low temperatures, absence of stirring or flow, and smoothness of walls—conditions exactly contrary to those in ore fissures. Nevertheless, some supersaturated solutions are remarkably stable. Zinc sulfide, for example, as pointed out by Glixelli (42), by Allen and Crenshaw (34), and by Kolthoff (8), is very insoluble in dilute acid; yet it precipitates so slowly that a quantitative separation can be effected from the more rapidly precipitating sulfides of Group II in the ordinary analytical scheme. That mercury sulfide may form dilute metastable solutions of the same sort is suggested by the persistent reports of its slight solubility in acids (see above, page 507). Thompson (2) proposes a mechanism based on supersaturation, to account for the selective deposition of cinnabar in shaly layers in limestone at Terlingua. Certainly there is no compelling evidence that supersaturation plays an important role in mercury deposition, but there is likewise no way of showing that such a mechanism is unreasonable.

Colloidal dispersions of mercury sulfide are easily prepared in solutions saturated with H_2S (Linder and Picton, 17), and sometimes appear despite precautions in ordinary analytical work. The colloidal sulfide has also been formed by mixing a sol of mercury and a sol of sulfur (Sauer and Steiner, 43; Sata, 44). In general, colloids should be relatively unstable under conditions met with in vein solutions—high temperature, high electrolyte content, continuous mixing, and rough walls. On the other hand, experiments on colloidal sulfides under such conditions have not been reported in the literature, and without experimental evidence colloidal transport cannot be ruled out. From the geological side the existence of quicksilver ore consisting of cinnabar finely dispersed through opal and chalcedony is possible evidence of transport as a colloid, perhaps stabilized by colloidal silica.

Pending further experimental work, supersaturation and colloidal dispersion must remain possible mechanisms whose importance in quicksilver transportation cannot yet be evaluated.

CONCLUSION.

Three possible mechanisms for the transportation of mercury in vein solutions stand up under detailed scrutiny: transportation as a complex ion in slightly alkaline sulfide solutions, as the volatile chloride, and as mercury vapor. For two other mechansims, supersaturation and colloidal dispersion, no definite statement can be made about their probable importance or lack of it. A sixth mechanism, transport in slightly acid solution as sulfomercuric acid, seems unlikely but cannot be altogether ruled out. Conceivable mechanisms depending on the solubility, ionization, or equilibrium reactions of H_2S, and on the stability of a complex halide ion, are clearly excluded.

The favored mechanisms most probably are all operative in quicksilver deposition, different ones predominating in different deposits, or in different stages of formation of any one deposit. The common separation of quicksilver deposits from most other sulfide ores is most easily explained by the instability of mercuric sulfide at moderate temperatures and the resulting transportation of mercury vapor itself. If the vein fluids contain abundant chloride, the vapor of mercuric chloride may accompany or replace the vapor of the metal. Deposition of cinnabar (or of native mercury or of chloride and oxychloride minerals) may take place directly from the vapor as the temperature falls; or if the vapor is entirely condensed to liquid, mercury can dissolve as the complex sulfide ion if the solution is slightly alkaline, or can remain in solution in a state of supersaturation or colloidal dispersion if the solution is neutral or acid. Deposition of cinnabar from such solutions may take place by any of several processes considered by Dreyer (1) and Thompson (2).

The objection is often raised in discussions of this sort that too many arbitrary assumptions must be made in order for the rules of physical chemistry to apply. To forestall such objections here, it should be emphasized that the laws of equilibrium have been used only to give ranges of possible values, to set gross limits on the reactions which may occur in cinnabar deposition. The actual figures in the tables have no meaning except as orders of magnitude. The laws of equilibrium can be applied as precise instruments in controlled experiments, or as blunt instruments in interpretations of natural phenomena; even used as blunt instruments they suffice to make certain possibilities and impossibilities abundantly clear. To assume for instance, that mercury can be appreciably soluble in the presence of sulfide at high temperatures because of the decreased solubility of H_2S, because of the decreased ionization of H_2S, or because of formation of a complex chloride ion, is completely unreasonable; the amount of mercury that could possibly be affected by such processes is too small by many orders of magnitude to have any importance in ore deposition. The system could be far from equilibrium, and our guesses about concentrations of ore solutions could be badly mistaken, and the conclusions would still hold. Likewise, Butler's suggestion that H_2S concentration in a vapor is kept negligibly small above 200° C by displacements of gas equilibria is clearly impossible; and the impossibility depends not at all on the strict accuracy of the chemical data, on the attainment of perfect equilibrium, or on the validity of our assumptions about gas

compositions. On the other hand, it is established beyond reasonable doubt that mercuric sulfide is appreciably dissociated into its elements at temperatures above 100° C, which means that mercuric sulfide *cannot even exist* in any system that includes moving vapors above a temperature of around 250° C (unless, of course, the vapors contain improbably high concentrations of gaseous mercury and sulfur); nor can the mercury exist at such temperatures in solution as a complex sulfide ion. This conclusion is not dependent on the attainment of complete equilibrium or on any guesses about conditions during ore deposition.

Thus equilibrium reasoning excludes some conceivable mechanisms of quicksilver deposition, and sets rough limits on conditions under which other mechanisms can act. To go beyond this point, to specify which of possible alternative mechanisms predominates in general and in particular deposits, is not the province of physical chemistry but of geology. An example of the application of geological evidence to such a problem is given in the paper by Thompson (2).

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A SENSITIVE FIELD TEST FOR DETECTING HEAVY METALS IN SOIL OR SEDIMENT.[1]

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ABSTRACT.

A semiquantitative colorimetric analytical method using nitric acid for digestion and dithizone for the determination is embodied in a simple test to detect the presence of copper, lead, zinc, and other nonferrous ore metals in soil or sediment. For the most part, only simple chemical equipment is necessary and tests can be made conveniently in a makeshift field laboratory. The test is adequately sensitive to obtain a slight positive test from the small traces of ore metals present in ordinary soils and sediments and can easily detect the larger quantities present in soils or sediments derived from ore deposits. It is hoped that the test will prove useful in prospecting for ore deposits by geochemical methods.

INTRODUCTION.

Ore deposits are generally surrounded by a geochemical anomaly or dispersion halo in which the ore-metal concentration is intermediate between that of the ore and that of the country rock. A "primary" halo genetically related to the ore deposit may occur in the unweathered country rock surrounding or overlying the ore. In addition, a "secondary" halo may be present in the rock-disintegration products: the soil, stream sediment, or dissolved salts that are derived from the weathering and erosion of the ore and any associated primary halo. Under favorable conditions it is possible, by chemical analysis, to detect the halo surrounding known ore deposits. It also may be possible, by the systematic use of chemical methods, to prospect successfully for new deposits. A prerequisite for successful geochemical prospecting is the development of analytical methods that are adequately sensitive and accurate for detecting and outlining the chemical anomalies and yet so rapid that it is feasible to analyze large numbers of samples. Fortunately, the range in metal concentration to be expected near ore deposits is large, and only a low order of accuracy is necessary for mapping the anomalies; advantage of this situation can be taken by sacrificing accuracy to simplify the chemical analysis.

The analysis can be considered conveniently as three steps: (a) sample preparation, (b) digestion, and (c) determination; and the field type of test differs from the accepted laboratory methods in that short cuts are taken in all three steps. In the field type of test it may be feasible to measure the amount of sample to be analyzed by means of a volumetric scoop and save some of the time required for weighing. The digestion can be simplified by using weaker acids for shorter periods of time than is customary in laboratory methods; and the determination can be simplified, in colorimetric analysis, by

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comparing with a few standards rather than using an optical colorimeter. All of these short cuts are utilized in the test described in this paper, and the results are compared with those obtained by standard laboratory methods to show that the short cuts do not obscure significant contrasts among the samples.

Field tests can be devised so that they are either specific for a certain metal or nonspecific so that they will give a positive reaction with any of a group of ore metals. Specific tests leave no doubt concerning the identity of the metal giving a positive test; they permit the distribution pattern of each metal present to be studied separately. Specific field tests for zinc in soils have been devised by Lakin, Stevens, and Almond (2) [2] and for copper and nickel in soils by Stevens and Lakin (6). Sergeev (5) gives other examples of specific field tests for metals in soil. Nonspecific tests seem to be especially useful in eliminating blank samples. In any broad-scale prospecting program the number of samples to be analyzed is likely to be very large, and most of the samples will be blanks; it would be of considerable advantage to dismiss these blank samples with a single analysis instead of making specific tests for each metal that might possibly be present. Thus, designing the test to be nonspecific, as has been done in the test described here, should be considered as another simplification.

Dithizone (diphenylthiocarbazone), the colorimetric reagent used in the field test described here, will detect small traces of the valuable metals found in sulfide ores but will not react with the common rock-forming metals. Thus, the use of dithizone avoids preliminary treatment for separating the common metals or preventing interference by them.

Dithizone is a violet-black solid that gives an intense green solution when dissolved in carbon tetrachloride. When the carbon tetrachloride solution of dithizone is shaken with a neutral aqueous solution containing one of the ore metals such as copper, lead, zinc, silver, mercury, cobalt, or nickel, a color change in the carbon tetrachloride phase will indicate the kind and amount of metal present. In many sulfide ores the amount of copper, lead, or zinc present greatly exceeds the amount of other metals present that will react with dithizone under the conditions of the test. The dithizonates of copper, lead, and zinc are bright red. Thus, when samples containing these metals are shaken with the dithizone solution the hue of the carbon tetrachloride phase changes from green through blue-green, blue, purple, red-purple, to red as the dithizone changes to metal dithizonate. The color changes are quite similar for each of the three metals or for any combination of them, which makes dithizone convenient to use in a nonspecific test.

The field test for soil and sediment is designed to supplement a previously described nonspecific field test for traces of heavy metals in water (1). The same dithizone solution is used for the determination in both tests, and much of the chemical equipment needed is identical. Depending upon their solubility, the metals from ore deposits, like all other rock disintegration products, may be discharged during weathering and erosion either mechanically by soil creep and sediment transport or in solution in ground and surface waters.

[2] Numbers in parentheses refer to Bibliography at end of paper.

The addition of a little more equipment to that needed for water analysis will enable detection of an ore metal in the erosion products regardless of how it is dispersed.

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PROCEDURE.

Sample Preparation.

Several possible choices present themselves in the collection and preparation of samples. Soil and sediment, especially if sampled in mountainous terrain, are likely to contain a high proportion of pebbles and cobbles. Most investigators would no doubt be inclined to discard the larger fragments but just where the separation should be made is a question. The writer has used the following two procedures for sample preparation:

A. Collect 100 to 500 grams of the material, dry, and sieve through a stainless-steel sieve with 2.0-mm openings. Crush fines in an iron mortar to a powder.

B. Collect 100 to 500 grams of the material, dry, and sieve through a stainless-steel sieve with 0.2-mm openings (80-mesh sieve). Do not crush.

Two possible alternatives are suggested for the method of measuring the amount of sample to be digested. Weighing the sample is accurate but is not as quick as measuring with a volumetric scoop. The writer usually uses a scoop having a capacity of 0.25 cu cm that is made by drilling a small cavity, which will hold about ⅓ gram of soil, in a plastic bar.

Equipment.

Dithizone (diphenylthiocarbazone) stock solution, 0.016 percent (weight/volume) solution in carbon tetrachloride. Prior to use of the method away from the laboratory prepare a supply of small glass vials, each containing 0.085 grams of solid dithizone. The solid dithizone is relatively stable. When needed, add the contents of one vial to 500 ml of carbon tetrachloride in a pyrex, paper-covered bottle. Shake vigorously to effect solution. Keep in a cool, dark place.

Dilute dithizone solution, approximately 0.0016 percent. Prepared by diluting 50 ml of stock solution to 500 ml with carbon tetrachloride. Adjust the final concentration of the dilute solution so that 5 ml will give a purple color when shaken with 2.5 micrograms of zinc under the conditions of the field test. Dithizone obtained from different manufacturers varies considerably in purity, and the writer has found it desirable to standardize the dithizone solutions by using zinc standards rather than by simply weighing the dithizone. The dithizone working solution is especially unstable. It should be kept in a pyrex, paper-covered bottle in a cool, dark place and should be discarded whenever comparisons with the zinc standard indicate that it is losing its strength. Webb and Millman (*7*, p. 7) describe special precautions that must be taken when working with dithizone in a tropical climate.

Carbon Tetrachloride. Purify by distilling in an all-pyrex still unless proved metal-free by testing with dithizone.

Water. Both tap and ordinary distilled water contain too much metal to be used. Purify by distilling in an all-pyrex still or by passing through a Model BD-1 Barnstead laboratory demineralizer or similar base-exchange device. For makeshift laboratories a Barnstead demineralizer cartridge can be used alone if it is arranged so that there is a slow, gravity-controlled flow of water through the cartridge. In many areas it is possible to find metal-free natural water that is a satisfactory substitute.

Concentrated nitric acid, approximately 69 percent (constant-boiling). Purify by distilling in an all-pyrex still.

Dilute nitric acid. Prepare by diluting 1 volume of concentrated acid with 7 volumes of water.

Hydrofluoric acid, approximately 48 percent. A.C.S. analyzed grade.

Ammonium hydroxide, approximately 1.0 *N*. Prepare by condensing ammonia gas in water and diluting. Some of the reagents required for the field test can probably be stored in soft glass instead of pyrex, but the ammonium hydroxide solution should be kept in pyrex.

Sodium acetate, 25 percent. Prepare by dissolving 250 grams of sodium acetate, or 415 grams of $NaAc.3H_2O$, in water; and purify by shaking in a large separatory funnel with dithizone stock solution and, after separation, remove traces of dithizone by shaking with pure carbon tetrachloride. Dilute to 1.0 liter.

Ammonium fluoride, 10 percent. Prepare by dissolving 100 grams of ammonium fluoride in water; purify as in the case of sodium acetate, and dilute to 1.0 liter. Keep in a pyrex bottle.

Buffer solution, containing 5 percent sodium acetate and 1 percent ammonium fluoride. Prepare as needed by diluting 200 ml of 25 percent sodium acetate solution and 100 ml of 10 percent ammonium fluoride solution to 1.0 liter in a wash bottle.

Standard zinc solution, 0.01 percent in approximately 0.1 *N* hydrochloric acid. Dissolve reagent-grade zinc in a slight excess of hydrochloric acid and dilute to volume. Before use, dilute with pure water and a little additional acid to a 0.001 percent solution (10 micrograms of zinc per ml).

Digestion tubes. Small pyrex test tubes (12 by 100 mm) with the rounded end drawn to a point as shown by figure 1a. The tubes are marked with a stylus to show a volume of 4.1 ml and with a letter so that they can be identified. Acid solutions tend to bump and spit when heated in ordinary round-bottom test tubes. In the pointed digestion tubes the acid solutions will boil steadily without bumping whether heated by a flame or by a hot plate. Upon heating, the solution boils just inside the tip of the tube; bumping will not occur as long as the solution in the tip boils before the main mass of the solution becomes superheated.

Digestion tube rack. The digestion tubes can be held conveniently in a wooden frame having a series of 13-mm holes spaced with centers about an inch apart.

Micropipettes. Micropipettes convenient for removing small aliquots of sample solution from the digestion tubes are prepared as follows: Draw one end of ¼-in. glass tube into a capillary and fire-polish the ends. Calibrate the micropipette by filling with the desired volume and marking at the meniscus. Pipettes having volumes of 0.2, 0.1, 0.05, 0.025, and 0.012 ml are required. A short length of rubber tubing on the large end of the pipette, as shown by Figure 1c, is useful for expelling the liquid.

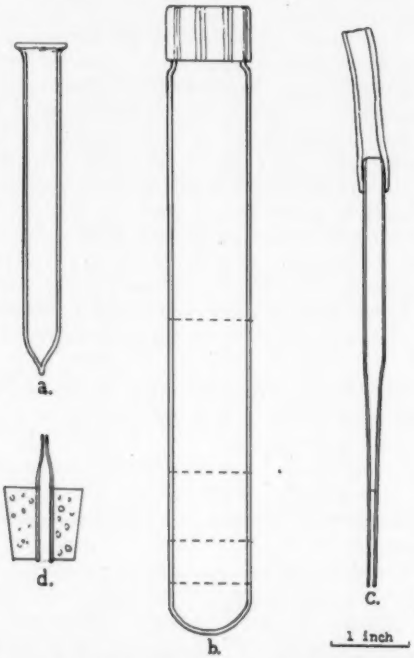

FIG. 1. Special equipment required for the heavy-metal field test: (a) non-bumping pyrex sample digestion tube prepared by drawing end of ordinary test tube to a point; (b) soft glass, screw-top culture tube marked at 5-, 10-, 20-, and 40-ml volumes; (c) micropipette for measuring small volumes of sample solution; and (d) bottle spout for dispensing dithizone solution.

Sample scoop. Plastic (lucite) bar containing a drilled cavity with a volume of 0.25 cu cm.

Colorimetric tubes. Glass culture tubes, 1 by 8 in., with a screw cap. Mark the tubes with a stylus at volumes of 5, 10, 20, and 40 ml. See Figure 1b. Clean tubes by filling with dithizone solution and inverting overnight. Glass-stoppered, graduated pyrex cylinders are a satisfactory substitute for the colorimetric tubes.

Other glassware. Graduates, beakers, burettes, cylinders, dropping bottles, separatory funnels, and pipettes. Glassware should be pyrex if possible.

Heating devices. Alcohol lamp, gasoline stove, electric hot plate (preferably thermostatically controlled).

Platinum dishes.

Cork for dithizone bottle. A cork with a small glass tube inserted in it as shown in Figure 1d will permit the dithizone solution to be dispensed without pouring carbon tetrachloride fumes from the bottle. Carbon tetrachloride fumes are toxic and the breathing of them should be avoided.

Digestion.

The proportion of copper, lead, and zinc extracted from a soil or sediment sample by an acid digestion depends upon the rigor of the digestion and how refractory the sample is. Four different digestion methods are described below which represent four distinct steps of increasing vigor of digestion. By the use of all four digestion methods on representative samples the digestion method best suited for use for a particular study can be selected; in general, the best method will be the quickest method that gives satisfactory results. Enough acid is used in each of the methods so that any limestone, dolomite, or other carbonate-rich material in the sample will be completely decomposed. Instructions for the digestions are as follows:

A. Place 0.33 gram (or a scoopful) of the sample in a digestion tube, add 4.0 ml of dilute nitric acid and heat over an alcohol lamp. Digest 10 to 15 samples simultaneously, boiling each in turn so that all are kept at or near the boiling point for 10 minutes.

B. Similar to A, but boil slowly and continuously on a hot plate for 1 hour. Add water to regain the 4.0-ml volume and mix by shaking.

C. Place the same amount of sample in a digestion tube, add 1.0 ml of concentrated nitric acid, and heat on a hot plate (low heat) overnight without boiling; heat further the following morning (high heat) until about half the acid is boiled away. Dilute to 4.0 ml and mix by shaking.

D. Place the same amount of sample in a small platinum dish, add hydrofluoric and concentrated nitric acids in equal amounts, making about 2.0 ml total volume, and heat on a hot plate at about 38° C until dry. The initial heating should take about 2 hours to dry the sample. Add two to five drops of concentrated nitric acid, and heat to dryness again. Add 10 drops (0.5 ml) of concentrated nitric acid and 10 drops of water, heat to dissolve sample, and wash into test tube with water. Dilute to 4.0-ml volume. Because of the acid fumes given off, this digestion should be performed under a hood or in a well-ventilated place.

Each of the four digestion methods leaves the sample dissolved in nitric acid of about the same concentration. When the sample solution cools, the solid residue settles to the bottom of the digestion tube, leaving a clear yellowish solution. Aliquots of this are pipetted for the determination.

Determination.

Place 5.0 ml of the dilute dithizone solution in a clean colorimetric tube, add 35 ml of the buffer solution, 0.2 ml of the sample solution, and shake for 30 seconds. Compare the color of the carbon tetrachloride layer with the color of similar layers prepared by using zinc standards or with the colors listed in Table 1 to determine the metal content of the sample (expressed as zinc equivalents, i.e., zinc plus one-half of copper plus one-fourth of lead). If the carbon tetrachloride layer is red or nearly red, clean the tube, using distilled water and dithizone solution; repeat the determination using a smaller aliquot of the sample solution. The object is to obtain a mixed color (red metal dithizonate plus unreacted green dithizone) after shaking so that the concentration can be determined by Table 1. The color differences are most sensitive near the purplish, midpoint of the range, and this range should be used for greatest accuracy.

TABLE 1.

TABLE FOR CALCULATING THE TOTAL HEAVY-METAL CONCENTRATION IN PARTS PER MILLION (EXPRESSED AS ZINC) OF SAMPLES FROM THE SIZE OF ALIQUOT USED AND COLOR OBTAINED IN THE DITHIZONE SOLUTION.

Aliquot (ml)	Volume of dithizone solution (ml)	Color						
		Green	Blue-green	Blue	Purple	Red-purple	Purplish-red	Red
0.2	5	0	50	100	150	200	250	300 or more
0.1	5	0	100	200	300	400	500	600 or more
0.05	5	0	200	400	600	800	1,000	1,200 or more
0.025	5	0	400	800	1,200	1,600	2,000	2,500 or more
0.0125	5	0	800	1,600	2,500	3,500	4,000	5,000 or more
0.0125	10	0	1,800	3,500	5,000	7,000	9,000	10,000 or more

Do not use more than 0.2 ml of the sample solution for the determination. The procedure as given is designed so that samples containing 50 or 100 parts per million (ppm) total heavy metal, a normal background concentration, will give a slight positive test and any concentrations higher than this background will be easily distinguishable. The test, as described, is not suitable for determining heavy metal contents in the range below 50 to 100 ppm, the normal background content. It is advisable to make many repeat determinations and to run blanks on the reagents frequently to avoid error by contamination. If any check determinations are to be omitted, omit those for "background" samples.

DISCUSSION.

Errors in Sample Preparation.—It is quite likely that large errors can be introduced in the process of sampling by selecting the wrong size-fraction of the soil for analysis. Ore minerals of copper, lead, and zinc tend to be softer than the common rock minerals and it might be hypothesized that these metals would tend to be concentrated, and would be most easily detected, in the fine size-fraction of the soil or sediment. A study of the behavior of copper in

alluvium at San Manuel (3) gives some support to this hypothesis, but more information is needed.

The writer usually uses the sample preparation method B described previously because it is somewhat simpler than method A and because it has worked satisfactorily wherever it has been tried. In the absence of more information it may be best to try both of the suggested methods and possibly others to determine the best procedure for any given area.

The error introduced by scooping rather than weighing the sample is easily determined. Samples from 10 different areas were measured by filling the volumetric scoop, tapping lightly to pack evenly, and leveling with a spatula. The scoopfuls were weighed, and the results are presented in Table 2. The results show that the error caused by scooping ranges from 3 to 11 percent and averages about 7 percent in any one area. The error is much

TABLE 2.

WEIGHT, IN GRAMS, OF SOIL SAMPLES MEASURED FOR ANALYSIS BY USING A SCOOP HAVING A VOLUME OF 0.25 CU CM.

Source of samples	No. of samples	Weight (grams)			Average deviation (grams)	Average deviation (per cent)
		High	Low	Average		
Coeur d'Alene, Idaho	17	0.25	0.14	0.18	0.020	11
Prescott, Ariz.	10	.31	.23	.27	.020	7
Platteville, Wis.	10	.30	.26	.28	.011	4
Tucson, Ariz.	10	.32	.24	.27	.022	8
Gold Hill, Colo.	10	.31	.26	.29	.017	6
Tiger, Ariz.	10	.31	.27	.29	.013	5
Blackbird, Idaho	16	.32	.20	.26	.025	10
Globe, Ariz.	10	.34	.29	.32	.010	3
Ward, Colo.	13	.37	.23	.32	.024	7
Tombstone, Ariz.	10	.33	.24	.28	.026	9
Average by districts	—	.32	.24	.28	.019	7.0
Samples from all 10 districts	116	0.37	0.14	0.27	0.037	14.0

larger if samples from different areas are grouped together. As the primary object in using the field test is to reveal differences among samples from one area, the error due to the scoop does not seem excessive. In fact, it seems to be considerably smaller than other errors of analysis, which will be described subsequently.

Reactions of Dithizone.—The reaction of dithizone with the various metals has been described in detail by Sandell (4) and by Welcher (8). The writer (1) summarized some of the pertinent information in describing a geochemical prospecting test for metals in water. Most soils contain considerable iron which dissolves when the soil is digested and which has a tendency to oxidize the dithizone during the determination. For this reason fluoride is introduced during the determination to suppress the iron activity and avoid the oxidation of the dithizone. It was necessary to make some experiments with standard solu-

tions, to be certain the dithizone reacted completely with copper, lead, and zinc in the presence of fluoride and under the conditions of acidity and buffer concentration that are recommended for the field test.

In Table 3, which presents the results of these experiments, the behavior of copper, lead, and zinc with dithizone is shown by the number of micrograms of the metal required to produce the purple color, indicating reaction with one-half of the dithizone present. It can be seen that the same reaction with dithizone is produced by different amounts of the various metals; twice the weight of copper and four times the weight of lead are required to produce the same effect as a given amount of zinc. Hence, the field test is most sensitive for zinc, less sensitive for copper, and still less sensitive for lead.

TABLE 3.

COMPARISON OF REACTIONS OF DITHIZONE WITH ZINC, COPPER, AND LEAD UNDER CONDITIONS USED IN FIELD TEST AND UNDER SLIGHTLY MODIFIED CONDITIONS. COMPARISON IS EXPRESSED AS THE NUMBER OF MICROGRAMS OF THE METAL REQUIRED TO PRODUCE THE PURPLISH MID-COLOR OF THE COLOR RANGE.

	Condition of test (see below)						
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Metal							
Zinc	2.5	2.5	2.5	2.5	2.5	2.5	3.5
Copper	5	5	5	5	5	5	5
Lead	11	14	20±	55±	15	20	20
Acidity (pH)	7.2	6.2	6.0	5.5	6.1	5.5	4.9

(1) Standard metal solutions plus 35 ml of buffer and 5 ml of dithizone solution as used in field test.
(2) Same as (1) plus 0.2 ml of dilute (1:7) HNO_3.
(3) Same as (1) plus 0.4 ml of dilute HNO_3.
(4) Same as (1) plus 1.0 ml of dilute HNO_3.
(5) Standard metal solutions plus 0.2 ml of dilute HNO_3 but with half-strength buffer (17.5 ml of buffer and 17.5 ml of water).
(6) Similar to (5) but with quarter-strength buffer.
(7) Similar to (5) but with eighth-strength buffer.

When the sample is digested in acid and an aliquot of the sample solution is removed for the determination, the amount of acid present varies depending both upon the size of the aliquot and upon the concentration of acid remaining after the digestion. If the sample is limestone or dolomite practically all the acid recommended for use in the field digestion will be consumed and even the largest aliquot used, 0.2 ml, will add little acid. If the sample consists mostly of inert silicates, however, the acid strength of the aliquot will approach that of the original acid. In Table 3, the greatest possible contrast in amount of acid added, under the conditions recommended for the field test, are given by columns 1 and 2. The results show that the recovery of zinc and copper are unaffected and the recovery of lead only slightly affected by the possible variations of acidity.

Columns 3 and 4 of Table 3 show that if the amount of acid for digestion is increased over that recommended the recovery of zinc and copper may be

unaffected but there may be a sharp decrease in the recovery of lead. In addition, columns 5, 6, and 7 of Table 3 show that if the amount of buffer for the determination is decreased from the recommended amount, there may be a decrease in the recovery of both lead and zinc.

These experiments indicate that it is possible to simplify the field test by using buffer alone to control acidity and obtain a satisfactory test for any of the three metals: copper, lead, or zinc. The test could easily be modified to increase the amount of acid used or decrease the amount of buffer, if provisions are made to add an indicator and neutralize with a base after digestion. The additional steps might improve the digestion but would slow the analysis. In order to simplify the process as much as possible the writer has elected to use the dilute acid and eliminate the neutralization. It is believed that the results, given at the end of this paper, further justify this simplification.

The extreme sensitivity of dithizone renders the test very susceptible to contamination. Before any determinations are made it is wise to check the purity of the dithizone solution and the reagents. The purity of the dithizone solution is checked by shaking with a dilute ammonium hydroxide solution known to be free of heavy metals. The dithizone should dissolve completely in the aqueous phase, leaving colorless carbon tetrachloride. Any pink tint left in the carbon tetrachloride indicates contamination by heavy metal; a yellow tint usually indicates a dithizone oxidation product. Any contaminated or oxidized solutions should be discarded. The reagents and apparatus can be tested by running blank analyses, which should produce no change whatever in the color of the dithizone solution. When it is established that the dithizone and other solutions are pure and the apparatus clean, the concentration of the dithizone solution can be checked by using the zinc standard.

Errors in Digestion and Determination.—The field test can be evaluated chemically by comparing the results of the field test with those from analyses of the same samples by established laboratory analytical methods. The error introduced by scooping samples can be eliminated by weighing the samples used for the field test in this comparison so that any errors in the results of the field test must be explained by errors in digestion or determination.

Tables 4, 5, and 6 give comparisons between field test and laboratory analyses of soil samples collected in a variety of mining districts. The samples have been selected so that Table 4 lists those with an ore-metal content that is dominantly copper, Table 5 dominantly lead, and Table 6 dominantly zinc. For field tests each sample was run by each of the four different digestion methods, to determine the effect of varying the intensity of the conditions of digestion, and each analysis was repeated once to determine the reproducibility of results. In order to make the study thoroughly objective, the repeat analyses were made on a different day and in such a manner that the analyst, Mr. J. P. Schuch, had no knowledge of previous results. It can be seen that the results of the field method agree fairly well with the laboratory determinations when the latter are expressed as zinc equivalents (zinc plus ½ copper plus ¼ lead). It is apparent that the field test will detect any of these metals if present in unusual concentrations.

TABLE 4.

COMPARISON OF RESULTS OF FIELD TEST WITH THOSE FROM LABORATORY ANALYSES OF SAMPLES RICH IN COPPER.
[ALL RESULTS GIVEN IN PARTS PER MILLION.]

Sample description	Laboratory analysis				Field Test			
	Copper	Zinc	Lead	Zinc equivalent	A	B	C	D
Soil, San Manuel, Ariz.	44	108	20	127	75; 100	100; 125	75; 75	100; 100
Soil, San Manuel, Ariz.	80	100	25	146	75; 50	100; 100	100; 100	125; 100
Soil, San Manuel, Ariz.	530	120	35	394	125; 100	225; 200	250; 250	450; 500
Soil, San Manuel, Ariz.	3,075	88	60	1,650	800; 800	1,600; 1,000	1,600; 1,000	2,000; 1,500
Soil, San Manuel, Ariz.	13,000	108	60	6,620	4,800; 4,000	4,800; 4,500	4,000; 5,000	6,500; 5,000
Soil, Blackbird, Idaho	100	—	—	50	75; 75	100; 100	100; 125	150; 150
Soil, Blackbird, Idaho	220	—	—	110	75; 75	100; 100	125; 150	200; 125
Soil, Blackbird, Idaho	440	40	10	262	125; 125	250; 250	125; 300	250; 200
Soil, Blackbird, Idaho	1,500	50	40	810	100; 300	400; 400	500; 500	500; 800
Soil, Blackbird, Idaho	3,000	170	10	1,670	800; 600	1,000; 800	1,200; 1,500	1,600; 1,600
Rock, Johnson, Ariz.	140	35	10	107	50; 50	75; 75	100; 100	125; 100
Rock, Johnson, Ariz.	410	35	10	242	100; 125	125; 125	300; 125	350; 275
Alluvium, Tucson, Ariz.	260	80	30	220	75; 75	125; 125	250; 200	200; 150
Alluvium, Tucson, Ariz.	610	80	20	390	200; 250	550; 400	500; 600	700; 400

TABLE 5.

COMPARISON OF RESULTS OF FIELD TEST WITH LABORATORY ANALYSES OF SAMPLES RICH IN LEAD.
[ALL RESULTS GIVEN IN PARTS PER MILLION.]

Sample description	Laboratory analysis				Field Test			
	Lead	Zinc	Copper	Zinc equivalent	A	B	C	D
Soil, Tiger, Ariz.	620	—	—	155	200; 200	350; 300	400; 400	400; 450
Soil, Tiger, Ariz.	850	—	—	212	200; 250	400; 450	500; 500	650; 700
Soil, Tiger, Ariz.	3,200	—	—	800	1,000; 800	900; 1,000	700; 700	1,600; 1.200
Soil, Tiger, Ariz.	3,400	—	—	850	800; 700	1,000; 900	1,500; 1,600	1,600; 1,600
Soil, Coeur d'Alene, Idaho	410	210	—	315	125; 150	200; 200	125; 125	200; 250
Soil, Coeur d'Alene, Idaho	4.300	530	—	1,600	800; 600	1,000; 800	900; 800	800; 1,200
Soil, Coeur d'Alene, Idaho	12,000	580	100	3,600	3,200; 2,400	4,000; 3,200	1,800; 1,800	1,600; 1,600
Soil, Platteville, Wis.	160	75	—	120	100; 100	150; 125	100; 100	200; 100
Soil, Platteville, Wis.	500	120	—	250	150; 125	175; 200	125; 300	250; 125
Soil, Platteville, Wis.	3,000	540	—	1,300	500; 800	800; 900	800; 700	1,200; 1,000
Soil, Platteville, Wis.	9,400	1,600	—	4,200	1,000; 2,000	2,400; 3,000	1,800; 3,200	3,200; 2,800
Soil, Platteville, Wis.	12,500	2,700	—	6,800	4,000; 4,200	4,500; 4,000	2,300; 3,600	4,800; 3,600
Rock, Tintic, Utah	720	70	25	260	100; 100	200; 125	100; 125	100; 125
Rock, Tintic, Utah	7,200	360	210	2,300	200; 400	800; 600	500; 400	1,700; 2,000

TABLE 6.

COMPARISON OF RESULTS OF FIELD TEST WITH LABORATORY ANALYSES OF SAMPLES RICH IN ZINC.
[ALL RESULTS GIVEN IN PARTS PER MILLION.]

Sample description	Laboratory analysis				Field Test			
	Zinc	Lead	Copper	Zinc equivalent	A	B	C	D
Soil, Platteville, Wis.	100	30	—	107	50; 75	75; 100	75; 100	100; 100
Soil, Platteville, Wis.	240	35	—	249	75; 150	100; 225	200; 175	300; 175
Soil, Platteville, Wis.	650	45	—	661	125; 150	250; 350	400; 600	700; 450
Till, Edwards-Balmat Dist., N. Y.	32	—	—	32	200; 50	150; 75	50; 50	75; 50
Till, Edwards-Balmat Dist., N. Y.	440	—	—	440	300; 125	400; 200	300; 250	300; 200
Till, Edwards-Balmat Dist., N. Y.	2,240	—	—	2,240	1,500; 1,500	1,500; 2,000	2,200; 2,200	2,000; 2,200
Soil, Friends Station, Tenn.	260	—	—	260	75; 100	75; 150	125; 200	200; 300
Soil, Friends Station, Tenn.	780	—	—	780	50; 75	200; 200	400; 800	650; 700
Soil, Friends Station, Tenn.	910	—	—	910	75; 75	225; 200	700; 700	900; 600
Soil, Friends Station, Tenn.	1,600	—	—	1,600	75; 50	800; 650	800; 1,500	1,200; 1,200
Alluvium, Tucson, Ariz.	80	30	18	96	75; 50	75; 75	75; 75	100; 75
Alluvium, Tucson, Ariz.	320	180	45	390	250; 250	200; 400	400; 300	300; 400
Rock, Tintic, Utah	120	25	20	140	75; 150	125; 200	125; 125	150; 125
Rock, Tintic, Utah	500	90	30	540	400; 400	500; 500	550; 500	400; 500

To facilitate comparison, the data from Tables 4, 5, and 6 are plotted as log-log graphs in Figures 2, 3, and 4. The results obtained by digestion methods A, B, and C are plotted against the average of the two analyses made by digestion method D, which represents complete digestion. The lines marked 100 percent and 50 percent are added to help evaluate the degree of extraction of the metals by the incomplete digestion methods. Thus, points

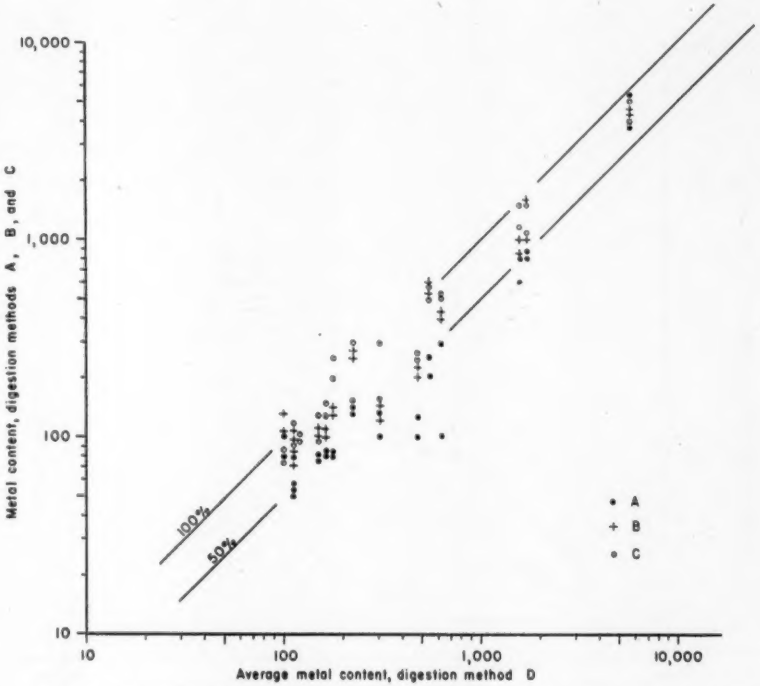

FIG. 2. Logarithmic comparison of results of partial digestion methods A, B, and C with thorough digestion method D for samples rich in copper (all results given in parts per million).

falling on the 100 percent line indicate complete extraction by the digestion method used and points falling on the 50 percent line indicate extraction of only half of the metal by the digestion method used.

It can be seen that repeated analysis of the same sample seldom gave identical results; yet the repeated analyses are commonly of the same order of magnitude and rarely differ by as much as 50 percent. Inasmuch as the treatment of the samples was identical for the repeated analyses it is assumed that

the errors indicated by these repeated analyses are random errors of determination.

In contrast to the random errors are the systematic errors caused by incomplete digestion. In many of the sample sets there is a progressive increase in extraction of the ore metals with progressive increase in rigor of the digestion. This variation is especially noticeable for samples difficult to digest, such as the soils rich in zinc from Friends Station, Tenn. For many such sample

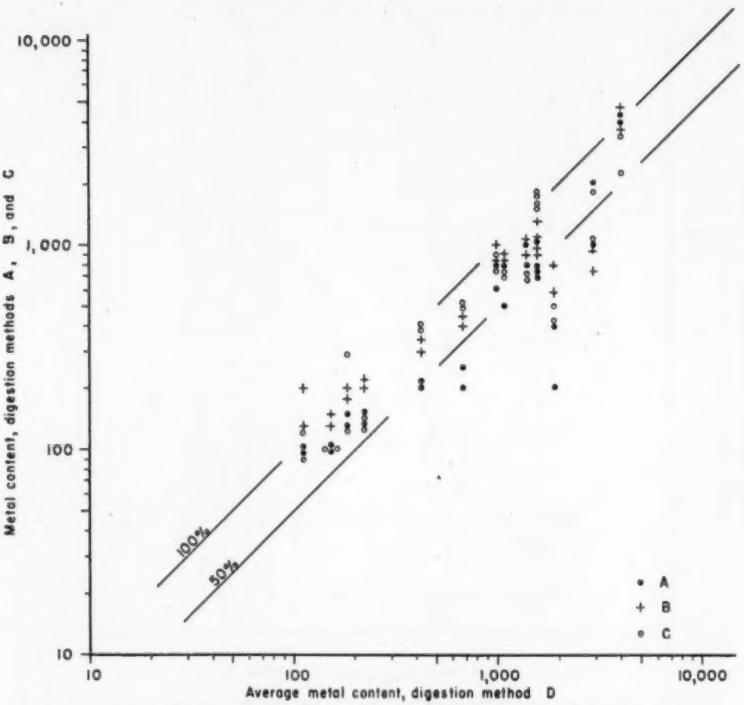

FIG. 3. Logarithmic comparison of results of partial digestion methods A, B, and C with thorough digestion method D for samples rich in lead (all results given in parts per million).

sets, the less rigorous digestion methods extract only a fraction of the metal content. Digestion method A gives the poorest results; it seems reasonable to conclude that this method should not be used unless it has been proved, by comparative digestion tests, to be satisfactory for the samples being analyzed. Digestion methods B and C work satisfactorily for most soil and sediment samples and for some rock samples but fail for other rock samples, as the rocks high in lead from Tintic, Utah.

Differences in digestion of the three metals—copper, lead, and zinc—seem to be much less marked than differences in digestion of various soil types. If a generalization can be permitted, it might be said that the desert types of soil are easiest to digest, immature soils from temperate climates are next easiest to digest, and the very old soils from temperate climates are most difficult to digest.

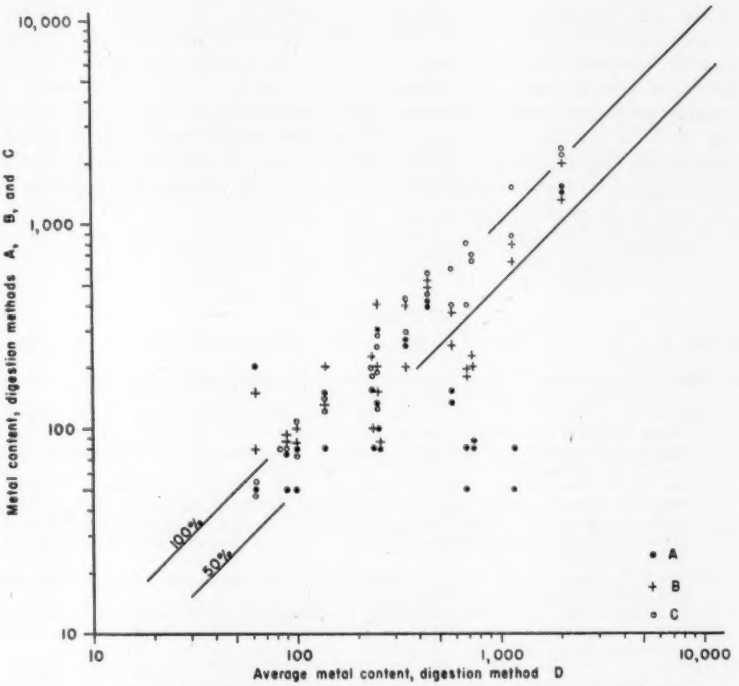

FIG. 4. Logarithmic comparison of results of partial digestion methods A, B, and C with thorough digestion method D for samples rich in zinc (all results given in parts per million).

The results indicate that the total error involved in the digestion and determination is large when compared with most colorimetric determinations and frequently amounts to as much as 50 percent. In comparison with this error, the error introduced by using a scoop instead of weighing out the sample is small. Fortunately, for the requirements of geochemical prospecting, the range of metal content in soils from the vicinity of an ore deposit is very large. The heavy-metal content of an ore may be as much as 1,000 times that of the country rock; the range of heavy-metal content to be expected in soil and

alluvium may not be nearly as large; but Tables 4, 5, and 6 show that it is commonly as high as 30-fold. The large analytical errors involved in the field test do not seem to detract appreciably from its usefulness in detecting or mapping geochemical anomalies of such magnitude.

CONCLUSIONS.

The field test for detecting heavy metals in soil or sediment is rapid, easy to run, and the equipment required is comparatively inexpensive. The test is sufficiently accurate to detect most of the significant abnormal or "higher-than-background" concentrations of heavy metals, whether the metal involved is copper, zinc or lead. The concentration in the sample can be determined roughly so that the heavy-metal anomalies can be mapped or contoured and the focus of the anomaly located. From the various methods of sample preparation and digestion described, the one can be selected that gives the quickest analysis that is satisfactory for the particular prospecting program.

U. S. GEOLOGICAL SURVEY,
GEOCHEMICAL PROSPECTING SECTION,
DENVER, COLO.,
February 18, 1951.

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THE KENTRON MICROHARDNESS TESTER, A QUANTITATIVE TOOL IN OPAQUE MINERAL IDENTIFICATION.[1]

FORBES ROBERTSON AND WILLIAM J. VAN METER.

ABSTRACT.

The Kentron Microhardness Tester combines pin-point placement of the indenter to one micron, with reproducible hardness values (within variable limits) on minute opaque mineral grains as small as 10 microns in diameter. The hardness range, in Knoop values, is from 5 to 1,500 for the opaque minerals examined. The hardness values and limits of hardness for 48 opaque minerals are given. Anisotropic minerals show variations in hardness with respect to orientation. Variable loads on the indenter result in variations in hardness values which are not fully explained. The instrument should be especially useful in the field of polished surface studies of the opaque ore minerals.

INTRODUCTION.

QUANTITATIVE hardness values for minerals have been determined by a number of methods. In the field of opaque mineral investigations, quantitative and semi-quantitative scratch tests of Talmage [2] and Murdock [3] are most commonly employed.[4] Quantitative indentation methods, first successfully developed by Brinell in 1900 and later by Vickers and Rockwell, are widely employed in metallurgical fields,[5] but their application to polished surface work on minerals has been limited. This is in part due, no doubt, to the fact that other, and less expensive methods of mineral identification, suffice, and that the more precise hardness data have been of limited significance.

One of the principal problems in opaque mineral determinations in polished surfaces is the mineralogy of very minute mineral grains. Many of the very small particles defy all but the most adept mineragraphic manipulators. The Kentron Microhardness Tester described in this paper couples quantitative hardness with pin-point placement of the indentation to a precision of less than one micron. Reproducible hardness values are obtained in mineral grains as small as 10 microns in diameter, or even smaller, dependent upon the nature of the mineral. The hardness range of the ore minerals, according to Knoop

[1] Kentron Microhardness Tester manufactured by Kent Cliff Laboratories, Peekskill, N. Y. Licensed by National Bureau of Standards to manufacture Knoop Indenter, Patent No. 2091995.

[2] Talmage, S. B., Quantitative standards for hardness of the ore minerals: ECON. GEOL., vol. 20, pp. 531–553, 1925.

[3] Murdock, Joseph, Microscopical determination of the opaque minerals, p. 28, John Wiley & Sons, New York, 1916.

[4] Short, M. N., Microscopic determination of the ore minerals: U. S. Geol. Survey Bull. 914, pp. 63–66, 1940.

[5] Kehl, G. L., The principles of metallographic laboratory practice, pp. 212–265, 1949, gives a good summary.

values, is from about 5 to 1,500, a broad scale consistent with the quantitative precision of the instrument. Winchell [6] indicated the possibilities of Knoop hardness in the field of mineragraphic applications, but did not enlarge upon this particular subject.

The purpose of this paper is to introduce this type of equipment to the field of opaque mineral investigation; to indicate its especial suitability for opaque mineral determinations; to present a preliminary series of Knoop values for about 48 of the ore minerals; and to demonstrate the possibilities and limitations of quantitative hardness values in mineral identification. Herein discussed are the range of values and the limits of precision of mineral hardness testing by this method.

KNOOP INDENTER.[7]

The Knoop Indenter, which is the heart of the Kentron Microhardness Tester, consists of a diamond crystal rigidly mounted in a metal holder. It is accurately ground to pyramidal shape, with the included longitudinal angle 172° 30′ and the included transverse angle 130°, as shown in Figure 1. The

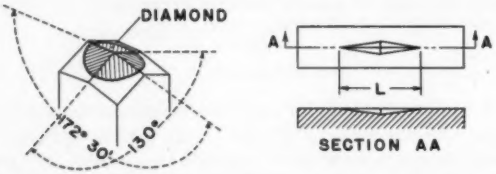

FIG. 1. Indenter (left). Knoop Indenter, showing the angles between the edges of the flat pyramidal diamond point. Indentation (right). Diagram of Knoop indentation. Ratio of length to width is 7:1. Ratio of length to depth is 30:1.

impression that results from this type of indenter is rhomboidal or "diamond-shaped," with the long diagonal approximately seven times the length of the short one and 30 times the depth of the impression. Figure 2 shows actual indentations in a mineral specimen.

Studies indicate that with this indenter the major part of the elastic recovery of the impression, upon removal of the load, will take place transversely rather than along the length of the impression. Consequently, by taking the measurement of the long diagonal only, a very close value of the unrecovered projected area can be computed, from which, the Knoop Hardness Number [8] is obtained and expressed by the formula

$$\text{K.N.} = L/Ap = L/l^2Cp,$$

[6] Winchell, H. N., The Knoop microhardness tester, a mineralogical tool: Am. Mineralogist, vol. 30, pp. 583–595, 1945.

[7] Knoop, Frederick, Peters, C. G., and Emerson, W. B., A sensitive pyramidal-diamond tool for indentation measurements: Jour. of Research, Nat. Bur. Standards, vol. 23, pp. 39–62, 1939.

[8] Op. cit., p. 46.

where K.N. = Knoop Hardness Number, L = the load in kilograms applied to the indenter, Ap = the unrecovered projected area of indentation in square millimeters, l = the measured length of the long diagonal of the indentation in millimeters, and Cp = the constant relating the projected area and dimensions of the indentation. The Knoop Hardness Number, corresponding to the measured length for a given load, may be read from a chart supplied with the instrument. The constant Cp is 7.028×10^{-2} for a theoretically perfect indenter. The constant can be corrected for any given indenter; however, to be acceptable in the Kentron instrument, the value must fall within narrow limits specified by the National Bureau of Standards.

KENTRON MICROHARDNESS TESTER.

The Kentron Microhardness Tester (Fig. 3) is a comparatively new instrument in the microhardness testing field. It provides a means for making hardness determinations with great accuracy according to well-known, and

FIG. 2. Indentations made with Knoop Indenter in galena. Approx. × 130.

widely accepted systems, principally Knoop and Vickers. Only Knoop values and the Knoop indenter were used in this investigation. The ease of operation and the extreme precision in placing an indentation at the desired location on the specimen are outstanding features.

The design of the Kentron provides for controlled rate of load application, so that the indenter may be impressed into the test specimen without detectable impact effect, and with a minimum possibility of fracturing brittle materials, an especially significant feature in mineral determinations. The rate of loading is variably controlled by means of a small hydraulic dashpot. A flexure plate beam suspension provides friction-free movement of the indenter loading beam during indentation, and thus assures the accuracy of loading essential to microhardness testing. The flexure plate type of beam suspension has the further desirable effect of causing the indenter to move through the same precise predetermined arc during each cycle of beam movement. The small angu-

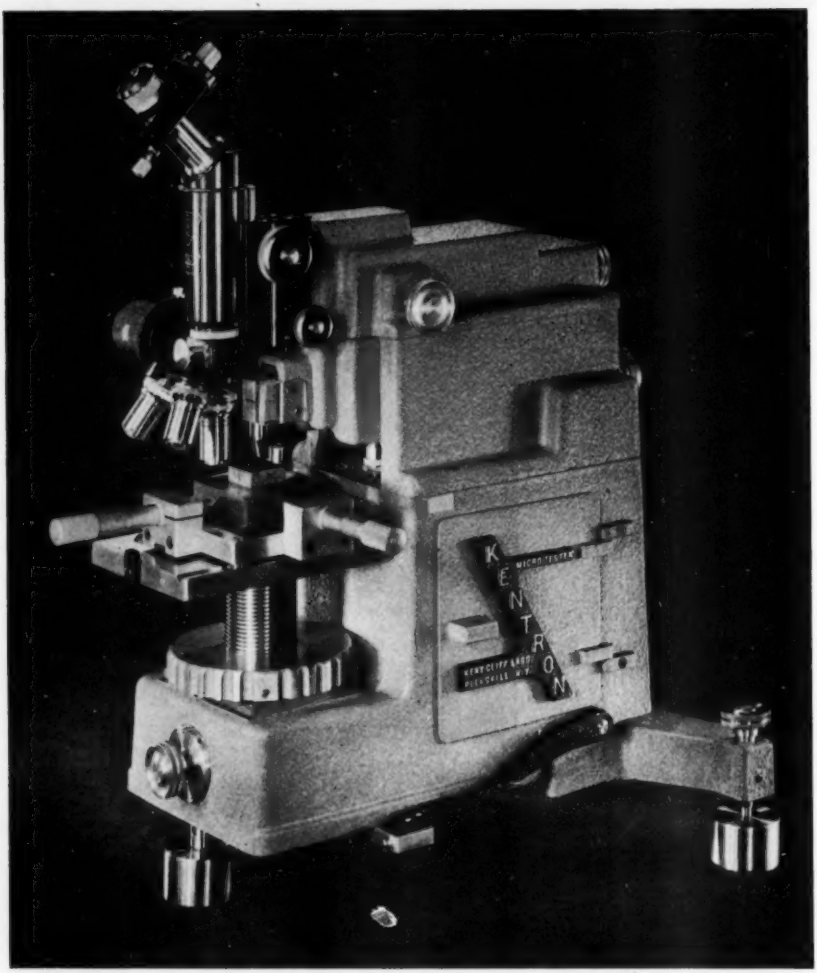

FIG. 3. Photograph of Kentron Tester.

lar value of the arc provides virtual straight-line motion of the indenter during indentation, which means that the point of the indentation is fixed with respect to the instrument base. This feature, in combination with the unique mechanical stage with its rapid and positive positioning, gives the operator absolute control in placing the indentation in a very small area.

Integrated into the Kentron instrument is a complete metallurgical microscope, which serves the dual purpose of enabling the operator to examine the specimen surface at the desired magnification in order to select the precise location for the hardness determination, and to measure the size of the indentation produced. To make a test, the area to be indented is brought to the center of the optical field by means of dual micrometers on the stage. Then, by a simple manual movement, the entire stage is transferred to the positively located "back" or "indenting" position. After the indentation has been made, the stage is returned to the positively located "forward" or "viewing" position. The indentation will appear in the center of the field and is measured by means of a filar micrometer eyepiece. The Knoop hardness value is readily determined by reference to printed tables. It is general practice to give the indenting load used as well as the Knoop number.

DISCUSSION OF RESULTS.

The limits of reproducibility within a given mineral species are indicated in the data presented in Table I, and shown graphically in Figure 4. The range of reproducibility observed is from 2 to 650 on the Knoop scale. In general, the lower the value, the more reproducible are the results both in low Knoop values and percentage-wise. However, some of the harder minerals show close reproducibility of results. For example, the chromite specimen used had an average hardness of 1,098, with a maximum deviation of 83 units.

Isotropic minerals of essentially constant composition give reasonably useful values. On the other hand, members of isomorphous series, or minerals which have limited compositional variations in solid solution, show variations which are thought to be due, in part, to the variable composition. Sphalerite from widely different districts and containing different amounts of iron gave a range in hardness which suggest that the higher the iron content, the harder the mineral. This is not, however, the whole story. Attempts were made to correlate hardness and iron composition quantitatively, but the insufficient data gave uncertain and erratic results.

Anisotropic minerals may show marked differences in hardness with respect to the orientation of the indentation with the crystallographic axes. By indentation hardness, molybdenite is nearly five times harder normal to the basal cleavage (pinacoid) than parallel to the cleavage. Stibnite, enargite, huebnerite, and teallite were specifically tested with the long axis of the indenter parallel to the long and short axes of the crystals in polished surfaces. The results indicate marked differences in hardness, and quite reproducible results for the long and short axes were obtained, although precise crystallographic orientations were not made. In the case of arsenopyrite, the crystallographic orientations were not taken into consideration and extreme variations in hardness from 633 to 1,148 were obtained.

Minerals are more difficult to work with than metals. It was found, for example, that many of the minerals have a tendency to chip at normal loads, and therefore require rather light loads for the indentations. Pyrite is especially difficult to work with and chips readily. This fact may account for the

Figure 4

LIMITS OF KNOOP HARDNESS NUMBERS FOR OPAQUE ORE MINERALS (LOGARITHMIC SCALE)

Mineral	Hardness Scales Mohs	Talmage	Knoop
GRAPHITE	1 -2	A	12 - 44
MOLYBDENITE	1 -1½	B-	12 - 60
ARGENTITE	2 -2½	A	26
REALGAR	1½-2	B	47
TEALLITE	1½	C	53 - 133
TELLURIUM	2 -2½	B , B-	54
CHALCOCITE	2½-3	B	58
DIGENITE	2½-3	B	70
COPPER	2½-3	B , B-	73
GALENA	2½-2¾	B	75
GOLD	2½-3	B	79
ANTIMONY	3-3½	B	89
BORNITE	3	B	98
BOULANGERITE	2½-3	B , B-	98
COVELLITE	1½-2	B-, B-	101
PYRARGYRITE	2½	C	103
JAMESONITE	2½	B , B-	126
STIBNITE	2	B	126
PLATINUM	4 -4½		132
SILVER	2½-3	B	143
ENARGITE	3	D-	154 - 378
CHALCOPYRITE	3½-4	C	168
SPHALERITE	3½-4	C-, C-	208
ALOOMDONITE	4	C-, C	218
CUPRITE	3½-4	D-	229
SYLVANITE	1½-2	C	234
PENTLANDITE	3½-4	D-	294
PYRRHOTITE	3½-4½	D-	296
TETRAHEDRITE	3 -4½	B	299
HUEBNERITE	5 -5½	E	313 - 464
COLUSITE	3 -4	C	331
WOLFRAMITE	5 -5½	E	370
MOTTRAMITE	3½	D	378
NICCOLITE	5 -5½	E	460
QUARTZ	7		467
GOETHITE	5 -5½	E	476
HAUSMANITE	5½	D-	493
MAGNETITE	5½-6½	F	536
PYRITE	6 -6½	F	577
HEMATITE	5 -6	G	698
FRANKLINITE	5½-6½	G	770
ARSENOPYRITE	5½-6	F-	811
MARCASITE	6 -6½	E-	818
SMALTITE	5½-6	F	837
ILMENITE	5 -6	G	965
MARTITE	5 -6		998
CHROMITE	5½	G	1093
BERTHIERITE	2 -3	D-	1148

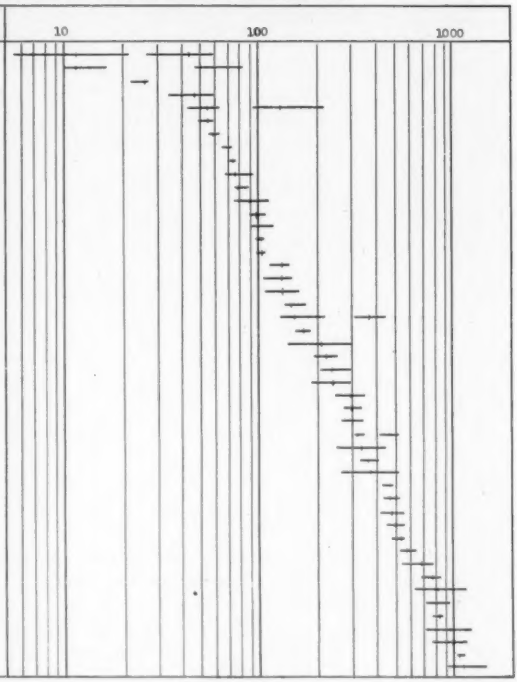

FIG. 4.

Hardness Values:

Mohs Scale from Palache, Charles, et al., The system of mineralogy, vol. 1, John Wiley & Sons, Inc., 1944, and Dana, E. S., and Ford, W. E., A textbook of mineralogy, John Wiley & Sons, Inc., 1926.

Talmage Scale from Short, M. N., Microscopic determination of the ore minerals, U. S. Geol. Survey Bull. 914, 1940.

Knoop Scale from best average values Table I. While it would seem ideal to tabulate hardness values for all minerals in the table from tests employing the same indenting load, practical considerations of grain size, hardness of individual minerals, and other factors preclude this. It is possible that some change in relative positions within the table for the minerals tested might take place were other employable loads used for certain specimens. For this reason, it is always preferable to note the load used when indicating a Knoop hardness value. Shifts in the positions of the minerals should likewise be anticipated when a considerably greater number of specimens are tested and more valid averages and limits become well established. The numerical values indicated must be considered as best averages from the data available, and thus are tentative only.

Shubrooks, G. E., Microhardness testing of small tools: Modern Machine Shop, p. 2, Feb. 1947.

TABLE I.

KNOOP MICROHARDNESS VALUES FOR SOME OF THE OPAQUE ORE MINERALS.

Mineral	Composition	Load in grams	Number of tests	Micron lengths			Knoop hardness values			Remarks
				Max.	Min.	Avr.	Min.	Max.	Avr.	
Algondonite	Cu_6As	100	5	86.5	74.8	80.8	190	254	218	
Antimony	Sb (native)	10	5	43.5	35.2	40.0	75	115	89	
Argentite	Ag_2S	50	5	169.5	163.4	165.5	22.1	26.7	26	
Arsenopyrite	FeAsS	100	5	47.4	35.2	41.8	633	1,148	814	
Berthierite	$FeS–Sb_2S_3$	10	5	12.2	10.2	11.2	956	1,368	1,134	Very small crystals
Berthierite		50	5	27.8	22.5	24.9	921	1,406	1,148	
Bornite	Cu_5FeS_4	100	4	127.5	113.5	120.5	87.5	110	98	
Boulangerite	$5PbS–2Sb_2S_3$	50	5	89.4	78.2	85.3	89	116	98	
Chalcocite	Cu_2S	100	6	161.0	149.5	156.5	54.9	63.6	58	
Chalcopyrite	$CuFeS_2$	25	5	48.4	42.5	45.1	152	197	175	Small blebs
Chalcopyrite		100	5	95.8	88.3	92.0	151	183	168	
Chromite	$(FeCr)_3O_4$	200	4	51.6	49.7	50.9	1,069	1,152	1,098	
Colusite	$Cu_3(AsSnVFeTe)S_4$	25	10	38.5	28.3	31.4	240	444	331	
Copper	Cu (native)	200	4	201	194	198	70.4	75.6	73	
Covellite	CuS	25	4	61.1	57.0	59.3	95	109	101	
Cuprite	Cu_2O	25	6	42.0	34.7	39.3	202	295	229	
Digenite	$Cu_{2-x}S$	100	7	148.5	140.0	143	64.5	72.6	70	
Enargite	$Cu_2S–4CuS–As_2S_5$	25	10	51.8	40.5	46.7	133	217	154	Longitudinal
Enargite		25	10	34.2	28.3	31.4	304	444	378	Transverse
Franklinite	$(FeZnMn)O–(FeMn)_2O_3$	100	5	45.4	40.5	43.0	690	868	770	
Galena	PbS	100	5	148	124	138	65	93	75	
Goethite	$Fe_2O_3–H_2O$	100	5	58.1	50.8	54.7	422	551	476	
Gold	Au (native)	10	5	43.9	40.0	42.5	73.8	88.9	79	
Graphite	C	2	17	71.8	21.9	41.0	59.3	5.5	25	
Graphite		2	10	71.8	37.1	50.7	5.5	20.7	12.5	Average of low values
Graphite		2	7	32.2	21.9	29	27.4	59.3	43.7	Average of high values
Graphite		5	6	77	24	44	12.3	123	43.3	
Hausmanite	$MnO–Mn_2O_3$	50	5	40.0	35.6	38	445	562	493	
Hematite	Fe_2O_3	300	5	89.5	73.3	78.2	533	794	698	
Huebnerite	$MnO–WO_3$	25	5	34.2	32.5	33.7	304	337	313	Longitudinal
Huebnerite		25	5	29.3	26.4	27.7	414	511	464	Transverse
Ilmenite	$FeTiO_3$	5	5	12.2	7.3	8.7	478	1,335	919	Small blebs in magnetite
Ilmenite		25	5	22.5	16.6	19.2	703	1,291	965	
Jamesonite	$4PbS–FeS–3Sb_2S_3$	50	5	79.3	70.0	75.2	113	145	126	

TABLE I—*Continued.*

Mineral	Composition	Load in grams	Number of tests	Micron lengths			Knoop hardness values			Remarks
				Max.	Min.	Avr.	Min.	Max.	Avr.	
Magnetite	Fe_3O_4	25	5	28.8	24.9	26.3	429	574	514	Small blebs in franklinite
Magnetite		100	5	54.1	49.8	51.5	486	574	536	
Marcasite	FeS_2	25	3	19.6	18.6	19.0	926	1,038	985	
Marcasite		200	4	63.2	54.5	59	712	958	818	
Martite	Fe_2O_3	50	5	30.3	24.4	26.7	775	1,195	998	
Molybdenite	MoS	10	5	119	94.8	109.3	10.1	15.8	12	Parallel to basal pinacoid
Molybdenite		10	5	54.7	42.0	48.9	47.6	80.7	60	Normal to basal pinacoid
Molybdenite		25	5	194	170	183	9.5	12.3	11	Parallel to basal pinacoid
Motramite	$2CuO–2PbO–V_2O_5–H_2O$	5	5	14.6	11.5	13.2	334	538	408	Small grains
Motramite		10	6	23.4	16.6	19.5	260	516	378	
Niccolite	NiAs	25	5	28.8	27.3	27.8	429	477	460	
Pentlandite	(Fe,Ni)S	25	5	38.6	31.3	34.8	239	363	294	
Platinum	Pt (refined)	25	5	58.6	46.4	51.9	104	165	132	
Pyrargyrite	$3Ag_2S–Sb_2S_3$	25	5	60.5	57.1	58.7	97	109	103	
Pyrite	FeS_2	100	6	44.5	41.3	42.4	719	834	792	
Pyrite		300	5	90.3	81	86	523	651	577	
Pyrrhotite	$Fe_{1-x}S$	25	5	37.6	35.2	36.5	252	287	267	
Pyrrhotite		100	6	72.3	65.2	69.3	272	335	296	
Quartz	SiO_2	100	5	57.7	51.8	55.2	427	530	467	
Realgar	AsS	25	5	100.5	77.7	86.7	35.2	58.9	47	
Silver	Ag (native)	50	5	72.8	65.9	70.5	134	164	143	
Silver		100	5	121	105	116	97.2	129	106	
Smaltite	$(CoNi)As_{3-x}$	5	5	10.6	7.7	7.3	633	1,585	823	
Smaltite		25	5	21.0	15.6	18	807	1,462	1,098	
Smaltite		200	5	60.5	57.2	58.3	777	870	837	
Sphalerite	(ZnFe)S	10	46	30.7	22.0	26.1	151	294	209	
Stibnite	Sb_2S_3	100	3	117	100	106	104	142	126	
Sylvanite	$Ag_2Au_3Te_8$	5	5	22.0	17.6	20.5	147	230	169	
Sylvanite		50	5	62.0	49.2	55.2	185	294	234	
Teallite	$PbSnS_2$	10	5	58.1	47.9	51.6	42.2	62	53	Longitudinal
Teallite		10	5	39.1	25.9	32.7	93	212	133	Transverse
Tellurium	Te (native)	10	5	53.7	48.8	51.5	49.3	59.8	54	
Tetrahedrite	$(CuFe)_{12}Sb_4S_{13}$	50	5	51.7	45.8	48.8	266	339	299	
Wolframite	$(FeMn)WO_4$	100	5	65.5	59.5	62.0	332	402	370	

wide range noted in the table. A few of the minerals show a tendency to "flow" rather rapidly and partially obliterate the limits of indentations before they can be measured. In addition, the thickness of the mineral, the hardness and proximity of the underlying mineral, the variable cushioning effect of the underlying mineral, voids, inclusions, and fractures influence the indentation, and these effects, in the majority of cases, cannot be evaluated with any degree of certainty.

Of special significance is the fact that very minute mineral grains yield quantitative hardness determinations which should be of great assistance in limiting the number of possible minerals that an inclusion might represent. For example, minute blebs of chalcopyrite in sphalerite were determined to have a hardness of 175 with 25 g load. The average hardness obtained for chalcopyrite is 168 with 100 g load. There is no possibility of confusion of the inclusions with harder, but somewhat similarly colored minerals such as pyrite or pyrrhotite, which have hardnesses of about 650 and 296, respectively. In many cases, this one quantitative determination should prove of great value in determining those minute mineral blebs which practically defy identification by routine methods. An examination of Figure 4 indicates the limited number of possibilities which a mineral might represent. As the list given includes about 20 percent of the opaque minerals found in ore deposits, the possibilities might be about five times as great as the actual number in Figure 4.

A series of indentations made from bornite across the mutual boundary with chalcocite indicate a distinct increase in hardness as the chalcocite is approached. The hardness variations may be due to compositional changes in the bornite; or a sloping chalcocite boundary beneath the bornite at very shallow depth; or both of these effects.

An effect which became apparent and which is not thoroughly explained is the fact that variations in load produce different hardness values. In general, values are higher for lighter loads, because the eye does not resolve the end points of the impressions perfectly, and a micron loss in a small length produced by a light load would be larger percentage-wise than in a greater length. This fact is recognized by the Bureau of Standards, who have given serious consideration to a recommendation that a flat increase of as much as three microns be made to all measurements. For homogeneous materials, such as the metals, this seems to make the values very nearly constant for all loads. In the experience with the minerals, however, such a flat increase will not correct all of the values. The lack of uniformity in composition of the mineral itself, impurities, voids, cracks, etc., including the sub-mineral topography on the underlying minerals—all have a bearing on the results.

In spite of the many difficulties in precision of reproducibility of results comparable to the precision of the instrument itself, the Kentron instrument appears to offer possibilities of obtaining very much more precise indentation hardness values than heretofore possible, and this precise determination should be of considerable assistance in the determination of unknown minerals.

A comparison of Knoop hardness values with Mohs and Talmage values is given in Figure 4. It is readily apparent that there are significant differences between scratch and indentation hardness in many instances. The lack

of quantitative agreement between Mohs and Talmage values is also conspicuous. A quantitative scale, such as the one partially developed, might serve to eliminate some of the problems in determining the hardness of minerals.

CONCLUSIONS.

Much more work must be done on the ore minerals from a quantitative standpoint before the full value of this type of instrument is known. The following tentative conclusions appear justified from the data accumulated thus far:

1. The opaque ore minerals lend themselves to precise hardness determinations which, for the individual species, vary in reproducibility. In the majority of cases investigated, the limits appear sufficiently narrow to be of considerable significance in contributing to a unique solution of a mineral unknown.

2. Anisotropism with respect to atomic packing and density, as well as compositional differences attributable to variable solid solution, influences the hardness determinations to variable degrees.

3. Minute mineral grains or inclusions yield as reliable hardness values as do the larger grains, a fact serving to limit the possible number of minerals for further tests.

4. Minerals offer a wide variety of problems in reproducible hardness determinations which are not so easily evaluated as similar problems in metals.

5. Light-load hardness values differ from the heavier loads, although partially correctable by a flat increase of as much as three microns for all measurements. However, other factors, as yet not fully evaluated, influence the variations. Although it would seem ideal to employ the same indenting load in all mineral determinations, practical considerations of grain size, hardness of individual minerals in a group, and other considerations noted herein, preclude this.

6. Scratch hardness and indentation hardness are not equivalents in many cases, especially in the harder minerals.

A full consideration of the last point involves very fundamental concepts in regard to the nature of the physical property described as hardness.

MONTANA SCHOOL OF MINES,
BUTTE, MONTANA,
AND
SANTA FE, NEW MEXICO,
January 25, 1951.

REVIEWS

Nonmetallic Minerals, Revised 2nd Edit. By RAYMOND B. LADOO AND W. M. MYERS. Pp. 605; figs. 18; tbls. 200. McGraw-Hill Book Co., Inc., New York, 1951. Price, $10.00.

This second edition is quite a different book from its 26-year old predecessor, both in appearance and content. It appears to have been almost entirely rewritten. It now provides a comprehensive coverage of all of the nonmetallic mineral substances used in industry, under ninety group headings. Under each mineral substance is given composition, general description, varieties, properties, occurrence, geographic distribution, production, and consumption, mining and milling, specifications, markets, and bibliography. All of the text material appears to be up to date, but the statistical tables end with 1946 or 1948 and of course these will soon be more out of date.

The book is bound to compete with *Industrial Minerals and Rocks,* the second edition of which was brought out by the American Institute of Mining and Metallurgical Engineers in 1949. The individual commodities do not receive as adequate treatment as in *Industrial Minerals and Rocks* since the latter covers 51 commodities in 1,156 pages and *Nonmetallic Minerals* covers 90 commodities in 605 pages (of smaller type). The index is only 5 pages compared with 45 pages in *Industrial Minerals and Rocks.* The advantage of *Nonmetallic Minerals* is the larger number of commodities covered. This volume will make a handy reference book for anyone interested in industrial minerals and is bound to find a place on the desks of such people.

Lagerstättenlehre, Ein Kurzes Lehrbuch von den Bodenschätzen in der Erde. By W. PETRASCHECK AND W. E. PETRASCHECK. Pp. 410; figs. 233; tbls. 8. Springer-Verlag, Wien, 1950.

This new volume by the two Petraschecks covers the field of ore deposits, nonmetallic minerals and rocks, salts, coal, and oil. The ore deposits section by W. E. Petrascheck is subdivided into general principles including magnetic, pegmatitic, pneumatolytic, hydrothermal, metasomatic, impregnation, veins, secondary processes, sedimentary and metamorphic processes, provinces, and connected features (44 pages). This is followed by descriptions of deposits of each metal and by a section on the methods of search for and evaluation of mineral deposits (150 pages).

The sections on industrial minerals, coal, and oil are by W. Petrascheck. The first covers the more important industrial minerals in haphazard order. The properties, origin, occurrence, and extraction of coal and oil are treated in the next two sections. A separate section by W. E. Petrascheck treats of salts and their formation and occurrence.

One gets the impression that the sketchy content is very much out of date—notably in relation to the treatment of oil and gas. Under the description of the Permian Basin of North America the Carlsbad potash deposits are not even mentioned. Only an occasional reference to the literature is given and these are mostly old or based on a few later German articles, which in themselves are mainly old.

It is obvious that little, if any literature in the English language of the last dozen years has been available to the authors. Most of the books and articles listed are 25 or more years old. Apparently all of the newer knowledge of economic geology has not yet become known to the authors. This book gives the impression of having been compiled from outdated books and might almost have been written twenty-five years ago.

Practical Oil Geology, Revised 6th Edit. By DORSEY HAGER. Pp. 589; figs. 227; tbls. 78. McGraw-Hill Book Company, Inc., New York, 1951. Price, $7.50.

This well known handbook appears in its 6th edition, the first one having appeared in 1915, and the 5th edition in 1938. The general arrangement of the last edition has been followed and the contents brought up to date. Among the new features one notices a revised section on evaluation of oil properties, new data on tectonics, modern well logging and well sampling methods, and a map of the deep basins of the United States favorable for oil.

The handbook is, as the title states, a practical book on the application of geology to the finding of oil and essential data relating to the occurrence, drilling, extraction, and character of oil and its relation to gas and water.

Like its predecessors it will be a handy book for the student and a general reference for oil men.

A Textbook of Geology. By ROBERT M. GARRELS. Pp. 511; figs. 301; tbls. 16. Harper & Brothers, New York, 1951. Price, $5.00.

This new textbook of geology is the eighth volume in Harpers Geoscience Series and it is claimed to be marked by important departures from the so-called standard style textbooks of geology. It is an analytical approach tried out for several years at Northwestern University. The book attempts to present an analytical rather than expository approach and is supposedly developmental rather than topical, with each chapter stemming from the preceding one. The author attempts, and has succeeded well, in presenting an understanding of geologic processes as opposed to listing their results or products. An example is the treatment of erosional processes under the heading of solar energy applied to earth materials. Although the subject matter is about the same as in all textbooks of geology there is a different arrangement and considerable integration. The use of graphs is rather striking.

The chapter treatments are as follows: 1, General Setting—the earth in space; 2, Surface Features; 3, Problem of the History of the Earth—cause and effect relationships; 4, Earth History from a Study of Running Water—stream work; 5, Work of Waves—considerable mathematical treatment; 6, Work of Wind; 7, Work of Ice—problem; 8, Water Underground; 9, Sedimentary Rocks—including geologic history from sediments; 10, Summary of Gradational Agents; 11, Igneous Rocks—including implications of geologic history; 12, Metamorphic Rocks; 13, Evidence of Earth Movement; 14, First Attempts at Earth History—a good chapter; 15, Final Examination of Age of Earth; 16, Interior of Earth; 17, True-Scale Models; 18, Mechanics of Earth Movement; 19, Origin of Earth; 20, Modern Life—living organisms; 21, Fossilization—preserval; 22, Survey of Geologic History—Paleozoic to Cenozoic; 23, Evidence of Evolution; 24, Mechanics of Evolution; 25, Interpretation of Geologic Environments, Reconstruction of a Typical Area—types of maps; 26, Origin of Man; Appendix I, Use of Graphs; Appendix II, Identification of Rocks and Minerals; Appendix III, Classification of Plants and Animals.

Although the chapter headings do not disclose all of the contents, the arrangement is interesting, and the illustrations are striking.

The book obviously will be widely used.

Structural Geology of North America. By A. J. EARDLEY. Pp. 624; figs. 343; pls. 16. Harper & Brothers, New York, 1951. Price, $12.50.

This unusual but awkwardly-shaped book with a double-column page, size 11¼ x 8¼ inches, is designed to carry larger illustrations, of which there are 750 combined in 343 figures. The book, however, does not fit in any of our bookshelves.

It is a monumental volume representing more than 10 years of work, and is the only one of its kind in the field. It is the ninth volume in Harpers Geoscience Series. It is the first work to describe the structural geology of an entire continent. It treats of mountain systems, basins, arches, volcanic archipelagos, erosion of highlands, and filling of basins. The content is equivalent to two good sized volumes.

The 35 chapters, except for the three preliminary and introductory ones, treat of the various structural areas and orogenies of the continent. The generous use of maps, cross sections, and block diagrams greatly clarify the text. Many maps are full page size and cross sections are the full page width of 11 inches. There are 16 full page paleotectonic maps in color. All of the illustrations are of good quality and the book is printed in large and legible type.

Although this volume is meant for advanced undergraduates it really is presented on a graduate student level. It should readily win first place as the outstanding advanced textbook on structural geology and a general reference for all geologists interested in regional and structural geology.

Optical Crystallography, 2nd Edit. By ERNEST E. WAHLSTROM. Pp. 247; figs. 217. John Wiley & Sons, Inc., New York, and Chapman & Hall, Ltd., London, 1951. Price, $4.50.

This new and expanded second edition has attempted to correct the faults of the 1943 edition and has been increased some 50 pages. The chief changes are general revisions and rewriting of many sections, an expanded and modernized list of references, an appendix on the Universal Stage, and redrawing of two-dimensional figures to three-dimensional illustrations in clinographic projection. This is a great improvement.

The 17 chapters deal with the fundamental principles of optical properties of crystals and of the polarizing microscope and accessories in determining the optical properties; the immersion method of index measurement is given considerable space.

The new edition is a considerable improvement over the first edition.

Possible Future Petroleum Provinces of North America. Edited by MAX W. BALL, ARTHUR A. BAKER, GEORGE V. COHEE, PAUL B. WHITNEY, AND DOUGLAS BALL. Pp. 358; figs. 153. American Association of Petroleum Geologists, Tulsa, Okla., 1951. Price, $4.00; $2.50 to members.

This valuable symposium, which gives an up-to-date picture of undiscovered oil resources, represents the work of 17 geological societies, 13 geological surveys, 33 oil companies, 8 universities, and 24 consulting geologists. It is, therefore, authoritative to the last word. The symposium was conducted by the American Association of Petroleum Geologists at its 35th Annual Meeting at Chicago, in April 1950.

After forewords by Max W. Ball and A. I. Levorsen, the volume covers the various potential oil regions, divided as follows: Alaska, by George Gryc, Don J. Miller, and T. G. Payne; Western Canada, by Alberta Society of Petroleum Geologists; Pacific Coast States and Nevada, by Pacific Section of American Association of Petroleum Geologists; Rocky Mountain Region, by Rocky Mountain Association of Geologists, Intermountain Association of Petroleum Geologists, New Mexico Geological Society, Wyoming Geological Association; Mid-Continent Region, by Tulsa Geological Society; West Texas and Eastern New Mexico, by West Texas Geological Society; Fort Worth Basin and Muenster Arch, North-Central Texas, by Fort Worth Geological Society; Downdip Mesozoic Rocks of South Texas, by South Texas Geological Society; Mexico, by Manuel Alvarez, Jr.; Mexico-Lower California, by Federico Mina; Western Gulf Coast, by Houston Geological Society; Continental Shelf of Gulf of Mexico, by Paul Weaver; Southeastern United States, by Committee of Geologists from the Southeastern United States; Northeastern United States, by Judson L. Anderson; Appalachian Region, by Appalachian Geological Society; Eastern Canada, by J. F. Caley, W. C. Gussow, I. W. Jones, D. J. MacNeil, W. A. Roliff, E. R. Rose, and A. E. Wilson; Eastern Interior Basin, by Illinois Geological Society and Cooperating Organizations. The major sections are subdivided into fields or regions, many of which are by separate authors.

This symposium includes the nine years of growth of knowledge since the 1941 symposium, particularly such items as the importance of reefs, continental shelves, and deeper beds. This volume includes nearly twice as many possible provinces as the 1941 symposium and excludes others.

The limitations are to basins of more than 1,000 feet of sedimentary section, up to 20,000 feet of depth of sediments with separate compilations below 20,000 feet, and the inclusion of unexplored areas within known oil and gas provinces if they have deeper possibilities.

The text of this book, with its many good figures and index maps, will be studied by all who are interested in the future development of oil in the United States.

Geography of the Pacific. OTIS W. FREEMAN, Editor. Pp. 573; figs. 156; tbls. 51. John Wiley & Sons, Inc., New York, and Chapman & Hall, London, 1951. Price, $8.00.

As stated on the jacket, this book by the Editor and 13 Pacific area specialists, covers "the ocean, the islands, the people, the resources, the industries, and other vital factors."

Everyone today wishes to learn more about the vast Pacific, which until World War II represented just about as vast a vagueness. Americans, particularly, knowing that they are guardians of the Trust Territories, will wish to learn more about these areas, which under Japanese domination were just as closed to outsiders as are the Iron Curtain countries today. Again, quoting from the jacket: "Beginning with a description of the geographic setting of the Pacific, the authors follow with discussions of the various native peoples and the explorations and settlement of the Pacific Islands in historic times. The environments of the islands of the Pacific and the continent of Australia are followed by descriptions of the human, economic and political geography. The closing chapter deals with the trade routes, local problems, and the possible future of the Pacific lands and peoples." This is the first book that has appeared to supply this need.

The chapter headings and the authors are: Geographic Setting of the Pacific, by Otis W. Freeman; The Native Peoples of the Pacific, by Kenneth P. Emory; The Exploration and Mapping of the Pacific, by Curtis A. Manchester, Jr.; Australia:

The Physical Framework, by Clifford M. Zierer; Australia: The Cultural Development, by Clifford M. Zierer; Northern Melanesia: New Guinea and the Bismarck Archipelago, by Robert G. Bowman; Eastern Melanesia, by John Wesley Coulter; The Mariana, Volcano, and Bonin Islands, by Neal M. Bowers; The Carolina Islands, by Curtis A. Manchester, Jr.; Micronesia: Marshalls, Gilberts, Ocean Island, and Nauru, by Leonard Mason; The Philippine Islands, by Joseph E. Spencer; Hawaii and American Island Outposts, by Otis W. Freeman; Eastern Polynesia, by Otis W. Freeman; Central and Western Polynesia, by Edwin H. Bryan, Jr.; New Zealand, by Robert G. Bowman; Indonesia, by Anthony E. Sokol; The Kuril and Ryukyu Islands, by Walter R. Hacker; Islands of the Eastern and Northern Pacific, by Otis W. Freeman; Trade, Transportation, and Strategic Location in the Pacific, by Charles M. Davis.

From the above list it will be seen that this book is of wide coverage and authoritative. The volume is an example of fine book making by Wiley and is nicely but not over generously illustrated. It is a book that should be read with interest by everyone who is not a geographer and of course students of geography must have it.

BOOKS RECEIVED.

CHARLES H. SMITH AND M. L. MIGNONE.

U. S. Geological Survey—Washington, D. C., 1950–1951.

Bull. 955-D. Gold Placers and Their Geologic Environment in Northwestern Park County, Colorado. QUENTIN D. SINGEWALD. Pp. 69; pls. 10; fig. 1. Price, $1.25. *Detailed descriptions of glacial and post-glacial events in relation to placers.*

Bull. 969-A. Diamond-Drill Exploration of the Dillsburg Magnetite Deposits, York County, Pennsylvania. PRESTON E. HOTZ. Pp. 25; figs. 4; tbl. 1; pls. 10. Price, 70 cts. *Replacement deposits in Triassic limestone conglomerate formed by a more fluid fraction resulting from the differentiation in place of a diabase sill.*

Bull. 969-B. Corundum Deposits of Gallatin and Madison Counties, Montana. S. E. CLABAUGH AND F. C. ARMSTRONG. Pp. 22; pls. 5. Price, 75 cts. *Corundum occurs in thin, lenticular layers of biotite-sillimanite gneiss. General geology and individual deposits described.*

Bull. 974-C. Frost Action and Vegetation Patterns on Seward Peninsula, Alaska. D. M. HOPKINS AND R. S. SIGAFOOS. Pp. 50; pls. 2; figs. 15. Price, 40 cts. *A study of the geomorphic significance of vegetation patterns as related to frost action at high latitudes and in areas of perennially frozen ground.*

Circ. 75. Selected Abstracts on Engineering Geology and Related Subjects. SEVERINE H. BRITT. Pp. 29. *World wide references.*

Cir. 86. Bibliography of U. S. Geological Survey Publications Relating to Coal, 1882–1949. LOUISE R. BERRYHILL. Pp. 52. *Includes supplementary list up to April 1951.*

U. S. Soil Conservation Service—Washington, D. C., 1950–1951.

Tech. Bull. 1026. The Bed-Load Function for Sediment Transportation in Open Channel Flows. HANS ALBERT EINSTEIN. Pp. 71; figs. 23; tbls. 8.

Describes a method of determining the bed-load function for many types of stream channels.

Rept. A-70.1. Studies of the Use of Pervious Fence for Streambank Revetment. JOHN T. O'BRIEN. Pp. 66; figs. 27.

Geology of Southwestern Santa Barbara County, California. T. W. DIBBLEE, JR. Pp. 95; pls. 17; figs. 6. California Div. Mines Bull. 150, San Francisco, 1950. *Detailed description of the stratigraphy, structure, and general geology. Describes also the Capitan, Lompoc, and Zoca oil fields, and diatomite, asphalt, and other deposits.*

Preliminary Report on the Geology of the Mt. Prospect Complex. EUGENE N. CAMERON. Pp. 44; pls. 11. Connecticut Geol. and Nat. History Survey Bull. 76, Hartford, 1951. *Three major groups of rocks: older metasediments and dioritic gneisses, granitic rocks and the younger mafic intrusives with contact metamorphism.*

Illinois Geological Survey—Urbana, 1951.

Rept. Inv. 148. Subsurface Geology and Coal Resources of the Pennsylvania System in Certain Counties of the Illinois Basin. Introduction. GILBERT H. CADY. **Clay County.** HEINZ A. LOWENSTAM. **Edwards County.** HENRY L. SMITH AND GILBERT H. CADY. **Gallatin County.** M. WILLIAM PULLEN. **Hamilton County.** MARY BARNES ROLLEY. **Richland County.** RAYMOND SIEVER AND GILBERT H. CADY. Pp. 151; figs. 30; tbls. 11; pls. 11. *Second of series of reports; the first was issued in 1944.*

Rept. Inv. 150. Illinois Mineral Industry in 1949. WALTER H. VOSKUIL. Pp. 63; figs. 14; tbls. 50. *Description material by material.*

Circ. 167. Aromatic Fluorine Compounds. II. 1, 2, 4, 5-Tetrafluorobenzene and Related Compounds. III. The Fluoromesitylenes and Derivatives. IV. 1, 2, 3, 5-Tetrafluorobenzene. V. 1, 3, 5-Tribluorobenzene. G. C. FINGER, F. H. REED, ET AL. Pp. 11. *Synthesis and properties; chemical.*

Circ. 173. Illinois Water Floods—A Summary. FREDERICK SQUIRES ET AL. Pp. 8; figs. 11.

Kansas Geological Survey—Lawrence, 1951.

Bull. 90, Pt. 2. The Geology of the Davis Ranch Oil Pool, Wabaunsee County, Kansas. R. KENNETH SMITH AND ELLIS L. ANDERS, JR. Pp. 39; figs. 6; pls. 2; tbls. 5. *Interpretations of the stratigraphy and structural relations of the Davis Ranch pool.*

Bull. 90, Pt. 3. Coal Resources of the Permian System in Kansas. WALTER H. SCHOEWE. Pp. 15; figs. 4; pl. 1; tbl. 1. *Noncommercial coal of local occurrence.*

Bull. 90, Pt. 4. Physical Properties of Eastern Kansas Crude Oils—A Preliminary Report. CHARLES F. WEINAUG. Pp. 7; fig. 1; tbl. 1. *Determination from 54 samples.*

Bibliography of Minnesota Geology. THEODORE G. MELONE AND LEONARD W. WEIS. Pp. 124. Minnesota Geol. Survey Bull. 34, Minneapolis, 1951. Price, $1.00. *Alphabetically by authors followed by index; up to date.*

Part I. Ohio Oil and Gas Well Drilling Statistics for 1950. Part II. Oil and Gas Production, History, Regulation, Secondary Recovery and Bibliography. ROBERT L. ALKIRE ET AL. Pp. 132; figs. 7. Ohio Div. Geol. Survey Rept. Inv. 8, Petroleum and Natural Gas Ser. 1, Columbus, 1951. *Reviews the drilling activity in Ohio during 1950, the history of oil and gas production, total wells drilled, geologic section and producing sands, discovery of petroleum, history of drilling regulations, secondary recovery, and a bibliography of petroleum and natural gas in Ohio.*

Oregon Metal Mines Handbook. By THE STAFF. Pp. 166; figs. 7. Oregon Dept. Geol. and Mineral Industries Bull. 14-D, Portland, 1951. Price, $1.25. *Mineral deposits of Northwestern Oregon; description by county.*

Volcanic Geology, Hot Springs, and Geysers of Iceland. TOM F. W. BARTH. Pp. 174; pls. 31; figs. 68; tbls. 55. Carnegie Inst. Washington Pub. 587, Washington, D. C., 1950. Price, $5.00 paper bound; $5.50 cloth bound. *Divided into four parts dealing with volcanism, hot springs, geysers, and descriptions of the various hot spring areas.*

Journal of Geological Education, Vol. 1, No. 1. Pp. 50. Assoc. of Geology Teachers, Appleton, Wisc., April 1951. Price, $1.15. *Description of courses in mineralogy by various teachers.*

Coal—Plant Life to Plastics. Bituminous Coal Institute, Washington 5, D. C. *In three parts: students' manual; memo to teachers; and book-box with specimens of various kinds of coal and coal products.*

On the Origin of Species. CHARLES DARWIN. Pp. 426. Philosophical Library, New York, 1951. Price, $3.75. *First reprint of the original edition of 1859; all other reprints have been made from partially expurgated later editions. This is Darwinism as originally written.*

Genesis and Geology. CHARLES COULSTON GILLISPIE. Pp. 315. Harvard University Press, Cambridge, Mass., 1951. Price, $4.50. *A lively account of the impact of scientific discoveries upon religious beliefs in the decades before Darwin; many furors took place before that over The Origin of Species.*

U. S. Steel Corporation—New York, 1951.

Venezuela and the Cerro Bolivar Iron Ore Deposit. FORBES CRONK. Pp. 10. *Ores mostly soft hematites, but top fifty feet are weathered hard limonite; drill hole samples show 63.50% iron; much has to be done to make exploitation possible.*

Future Supplies of Iron for the U. S. Ferrous Industry. R. H. B. JONES. Pp. 22; figs. 9. *Explanation of figures followed by brief descriptions of each source.*

Testing of Iron Ores and Agglomerates Related to Blast Furnace Use. R. J. MORTON AND J. L. YAKE. Pp. 32; figs. 7; tbls. 9. *Attempt to develop significant testing procedures.*

Hawaiian Volcano Research Association—Honolulu, T. H., 1949–1950.

4th Rept. Steam Blast Volcanic Eruptions. T. A. JAGGAR. Pp. 137; figs. 41. *Study of Mount Pelée in Martinique; comparisons with other volcanoes; theoretical conclusions.*

5th Rept. Abrasion Hardness. T. A. JAGGAR. Pp. 43; pls. 6; figs. 5; tbls. 7. *Scratch hardness tester; malacometry; tests at high, medium, and low speeds; discussion of abradibility. Object of research to design simple instrument for many uses.*

A Report on Japanese Natural Resources. Pp. 559; figs. 97; tbls. 115; maps 9; lists 4. Prepared in General Headquarters, Far East Command, 1948. *Exhaustive report including food, power and fuel, fiber sources, nonmineral construction materials, construction minerals and industrial raw material resources and requirements; possible advances in the efficiency of resource utilization in Japan and associated problems; glossary of terms; summary shows that Japan must depend on much imports.*

Phosphate Deposits of Angaur Island, Palau Islands. EARL M. IRVING. Pp. 99; pls. 12; figs. 3; tbls. 10. Military Geology Branch of U. S. Geol. Survey for General Headquarters, Far East Command, May 1950. *Four types of ore: nodular, oölitic, rock phosphate, mainly as subaerial deposits, and earthy, in depressions below the water table; thickness of deposits between 1 to 17 feet; as of 1948 1.10 million long tons minable reserves estimated; average composition 35% P_2O_5, 53 to 58% CaO.*

Ontario Department of Mines—Toronto, 1951.

Ind. Min. Circ. 2. Silica in Ontario. D. F. HEWITT. Pp. 16; figs. 2. *Important nonmetallic resources but not fully exploited; description of individual deposits.*

56th Annual Report, Vol. 56, Pt. 6, 1947. Geology of the Olden-Bedford Area. W. D. HARDING. Pp. 100; figs. 6; photos 17; colored geol. map, scale, 1″ = 1 mi. *In Grenville subprovince. Greywacke, quartzite, and limestone intruded by gabbros, and granite. Mineral occurrences described include apatite, asbestos, barite, brucite, corundum, feldspar, gold, graphite, iron, lead, mica, molybdenum, and zinc.*

59th Annual Report, Vol. 59, Pt. 3, 1950. Natural Gas in 1949. Petroleum in 1949. R. B. HARKNESS. Pp. 91; tbls. 17; figs. 1; graphs 4.

P. R. 1951–2. Preliminary Report on the Geology in the Vicinity of Aeromagnetic Anomalies on the Bancroft and Coe Hill Sheets. E. M. ABRAHAM. Pp. 19; figs. 2. *A tabular description of 87 anomalies caused by disseminated and massive magnetite of fair to no economic interest.*

P. R. 1951–3. Preliminary Report on the Geology of Clarendon Township, Frontenac County. B. L. SMITH. Pp. 6; maps 1, scale 1″ = 2 mi.

P. R. 1951–4. Preliminary Report on the Geology of South Canonto and Parts of Palmerston and Lavant Townships, Frontenac and Lanark Counties. B. L. SMITH. Pp. 4; map 1, scale, 1″ = 2 mi.

Map 1950–3. Township of McElroy. Scale, 1″ = 1,000′; in color.

Map 1951–1. Township of Carr. Colored; scale, 1″ = 1,000′.

Map 1951–A. Geological Map of Dome Township, District of Kenora, Ontario. Scale, 1″ = ½ mi.

Map 1951–B. Geological Map of Township 29, Range XIV, District of Algoma, Ontario. Scale, 1″ = ¼ mi.

Quebec Department of Mines—Quebec, 1950.

Geol. Rept. 35. The Geology of Eastern Gaspé. H. W. McGERRIGLE. Pp. 168; figs. 3; pls. 17; maps 8; cross sections. *General geology by period; stratigraphic relations; igneous geology and economic geology. Petroleum found is of good quality, but not established if commercial.*

Geol. Rept. 45. Marl Deposits of the Province of Quebec. G. W. WADDINGTON. Pp. 127; pls. 4; plans 52. *Description of each township; 154 samples analyzed.*

International Tin Study Group—The Hague, 1950.

A Statement on the Position and Prospects of the Tin Industry. Pp. 56; numerous tables. Price, $1.00.

Tin 1949–1950.—A Review of the World Tin Industry. Pp. 55; charts 2; appendices 8. Price, 50 cts. *Account of main development in production, consumption, economics of tin and tinplate industry.*

Economic Notes and Statistics, Vol. 3, No. 3. Pp. 31. Australia Bur. Min. Resources, Geol. and Geophysics, Victoria, 1951. *Australian antimony supplies, by H. F. Pearson; International Tin Conference, Geneva, 1950, by J. A. Dunn, and other data.*

Société Géologique de Belgique—Liège, 1950.

Granites et Minéralisation au Maniema, Congo Belge. N. VARLAMOFF. Pp. 59; figs. 14; pls. 3. *Age of granites still indefinite but probably post-Urundi and pre-Lindi; surrounding the granites are important deposits of cassiterite, wolfram, columbo-tantalite and gold; injections of aplite, pegmatite, and quartz.*

Aspects Particuliers du Wolfram du Gisement des Montmins, Allier, France. PIERRE EVRARD. Pp. 11; figs. 3; microphotos 7. *The wolfram deposit of Montmins appears in successive zones mixed with quartzo-feldspathic material; kaolinization results from pneumatolitic alteration connected with granite differentiation; important kaolin deposits; washing of kaolin shows cassiterite, monazite, xenotime, neotantalite, and topaz; hypothesis offered is of fractionated and rhythmic crystallization amidst successive injections of residual solutions.*

Les Gîtes de Manganèse du Domaine Atlasique au Maroc Français et leur Classification Géologique. J. WESTERVELD. Pp. 28; map 1. Geol. Inst. of Amsterdam Univ., 1951. *Occurrence and classification of the manganese deposits of French Morocco and comparison with those of Bulgaria and Asia Minor, Cuba, United States, Mexico and Chile. Develops a threefold classification: 1) Deposits of silver-poor manganese associated with volcanism during Late Cretaceous and Tertiary; 2) Rhodochrosite bodies associated with silver veins; 3) Concordant lenses in Mesozoic rocks of geosynclines.*

Departamento Nacional da Produção Mineral—Rio de Janeiro, 1949–1950.

Bol. 84. Mina de Galena Argentifera de Panelas de Brejauvas. MILCIADES Y. GUARANYS AND ALBERTO I. VELASCO. Pp. 116; numerous illustrations. *Geology and genesis of the deposit; outline of exploitation project; metallurgy.*

Bol. 86. As Perspectivas da Mineração no Brasil. MARIO DA SILVA PINTO. Pp. 40; numerous illustrations. *Good résumé of Brazil's mineral resources; more intense exploration and exploitation urged, specially for strategic minerals.*

Atividades do Departamento em 1948. MARIO DA SILVA PINTO. Pp. 83. *Yearly report of the Director.*

Sobre a Metalogenia do Urânio em Portugal. ALBERTO CERVEIRA. Pp. 47; figs. 6. Portugal Geol. Soc., Porto, 1950. *Uraniferous ore deposits of greater economic value and extension correspond to epithermal quartz veins and are epithermal; localized in Beira Baixa and Beira Alta, in strongly eroded regions, and occupying center of large granitic batholith; veins from 0.5 to 2 m, averaging 0.5% U_3O_8; presupposed of economic interest.*

Schwefel in Schlacke und Schlackenwolle. W. FISCHER AND S. WOLF. Pp. 231; figs. 2; tbls. 53. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, 1951. Price, DM 25.00. *Detailed investigation of the occurrence and combinations of sulfur and sulfides in slags, clinker, and mineral wool; also other elemental and mineral constituents and their properties.*

SCIENTIFIC NOTES AND NEWS

C. O. SWANSON, chief geologist of The Consolidated Mining & Smelting Company of Canada, Ltd., has been awarded the Blaylock Medal for distinguished service to Canada in the field of geology. The medal, given by the Canadian Institute of Mining & Metallurgy, was presented at the annual meeting in Quebec.

BRUCE KENNEDY, of Lansing, has resigned as Michigan state geologist and assistant mine appraiser with FRANKLIN PARDEE. He has accepted a position with Pickands, Mather & Company and will be located at Ironwood. HARRY J. HARDENBERG, division economic geologist, has succeeded Kennedy.

The Oil possibilities of South Central Wyoming were investigated August 1, 2, and 3, when more than 200 geologists, representing most major oil companies as well as state and federal agencies, gathered in Sinclair, Wyoming, for the Sixth Annual Field Conference of the Wyoming Geological Association. The program included transportation of participants in a 65 car caravan to various points of geologic interest in a 4,200 square mile area, of which less than 12 square miles now produce oil or gas. General Chairman of the Conference was R. W. Mallory, Stanolind Oil and Gas Company geologist. W. F. Brinker, Cities Service Oil Company, and Dr. D. L. Blackstone, Jr., were joint editors of the 200 page Guide Book which was prepared, and George Veronda, Ohio Oil Company, was in charge of caravan arrangements.

The Department of Geology, University of Kansas, announces the appointment of two new staff members. WILLIAM W. HAMBLETON will serve as Assistant Professor of Geology, teaching petrology and economic geology; he was Shell Fellow in Geology at the University of Kansas and received his doctorate this June. JOHN IMBRIE has been appointed Assistant Professor in Geology to teach paleontology and stratigraphy; he received his doctorate degree this June at Yale where he has been serving as Shell Fellow.

B. B. BROCK has returned to Vancouver after an absence of seventeen years with the Anglo-American Corporation in Africa.

G. S. HUME, Director-General of Scientific Services, Department of Mines and Technical Surveys, Ottawa, was elected Vice-President of the Geological Association of Canada at the Annual Meeting held in Toronto in March.

The Midwest Federation of Mineralogical Societies held their annual conference at the Michigan College of Mining and Technology in June. About 200 geologists and mineralogists from eight states attended. There were also field trips through the Keweenaw Peninsula.

R. W. THOMAS, general manager of the Ray Division of Kennecott Copper Corporation, has retired after 39 years' service with the division. He will remain until the end of the year in an advisory capacity. A. P. MORRIS, assistant general manager at Ray since September, will succeed Mr. Thomas, who had been general manager for 22 years.

J. A. CARPENTER, who was 25 years with the Mackay School of Mines, retired at the end of the school year.

LOUIS WRIGHT FERGUSON resigned from E.C.A. as engineer in charge of African mineral observation. He has taken the position as chief of exploration and mineral development for Casa Americana in Angola, Portuguese West Africa.

OLIVER B. HOPKINS, vice-president, Imperial Oil Ltd., and director of petroleum division, Department of Defense Production, has been named president of the Canadian Institute of Mining and Metallurgy.

JAMES T. KEMP is on leave from the American Brass Co., San Francisco, and is on the staff of the Defense Minerals Administration, Bureau of Mines, Washington, D. C.

TOM LYON has been named chief of the copper branch of the Defense Minerals Administration.

T. NISHIWAKI, chief geologist of Kamioka Mining and Smelting Co. (formerly Mitsui Co.) of Tokyo, Japan, is visiting American and European mining districts.

EARL IRVING has returned temporarily to Washington from the Philippines where he has been engaged with the work of the U. S. Geological Survey, Military Unit, Pacific Division.

T. S. LOVERING, of the U. S. Geological Survey, was in Washington, D. C., during June working with the President's Materials Policy Commission. He has been transferred to the Denver office and left for there in July.

GUY RIDDELL returned to his offices at Royal Oak, Md., and Washington, D. C., after lode and placer examinations in Nevada, Arizona, and California.